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By
Jeffrey C. Gillen,
Captain, USAF, BSC

A thesis submitted in partial fulfillment
of the requirements for the
Master of Science Degree.
South Dakota State University

1995

Modeling the Fate and Transport of TNT in Soils

This thesis is approved as a creditable and independent investigation by a candidate for the Master of Science degree and is acceptable for the meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ABSTRACT

Modeling the Fate and Transport of TNT in Soils

Jeffrey C. Gillen

June 5, 1995

The model, BIOROOT, was implemented as a predictive tool to assess the fate and transport and to determine the effects of vegetative remediation anticipated during remediation of trinitrotoluene (TNT) contaminated soils. The model is designed to incorporate biological, physical, chemical, and environmental factors in predicting the degradation fate of trinitrotoluene (TNT). Lagoons from an explosives washout facility at the Umatilla Depot Activity near the city of Hermiston, Oregon were utilized to illustrate the model. Four scenarios were simulated: 1). no degradation of the TNT contaminant, 2). degradation half life values of 1 year, 3). amending the soil with 10% organic material, and 4). initiating vegetative remediation using the alfalfa plant. The amount of contaminant leached from the upper soil matrix after 1300 days was 7300 g, 1400 g, 18 g, and -50 g TNT respectively. Vegetative remediation demonstrated an ability to prevent TNT from entering the soil-water phase and leaching into the ground water. Vegetation was also capable of capturing and remediating contaminant not in direct contact with the root system. Key words: remediation, vegetation, model, TNT, munitions, wastes.

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CHAPTER 1.

INTRODUCTION

Today, there are numerous hazardous waste sites in almost every state that are contaminated from explosive compounds. The U.S. Army has been charged with initiating and overseeing a large research and development program focused on finding remediation solutions to the environmental problems caused from munitions manufacture, maintenance, and disposal operations. The predominant problem exists at former army ammunition plants operated during the past century. The total quantity of contaminated soil at these ammunition plants has been estimated to approach 1 billion tons (Majors et al. 1994). As of 1986, there were only six ammunition plants that manufacture or conduct load, assembly, and packing operations with explosive compounds such as trinitrotoluene (TNT). These plants produced 1,900,000 pounds of TNT monthly. Maximum production capabilities were conservatively estimated to be at least 15 times the current production level (Roberts, 1986). During the past century, the U.S. Army estimates that approximately one billion tons of soil are contaminated from explosive compounds. The contamination at ammunition plants exists at concentrations averaging less than 200 ppm (Majors et al. 1994).

SCOPE OF THE PROBLEM

Three major industries are affected by explosive wastes: the military,

munitions manufacturing, and mining. The military is significantly impacted due to its diverse applications of explosives and munitions. Operational activities such as weapons maintenance and disposal produce the majority of the contamination problems. Almost every military installation has a weapon storage area where routine maintenance and disposal activities are performed.

Maintenance operations often produce waste streams known as "pink waters" due to its characteristic color. Pink waters are wastewaters generated during loading, packing, handling, and disposal operations. For instance, disposal operations may use hot water to remove the explosive from the bomb / shell casing. The mixture of disposed explosive in the wash water turns a pinkish hue when exposed to light. Historically, disposal activities placed unserviceable units into a dedicated trench and were remotely detonated. This trench, commonly known as a burn pit, was often nothing more than an open ditch located on a remote section of the base.

Manufacturers, including the pyrotechnics and fireworks industries, are primarily impacted from the effluent created during the production and purification of explosives. The purification of TNT generates a waste stream known as "red water" due to its characteristic color resulting from sulfite reactions with the explosive impurities. Finally, the mining industry is impacted from explosive residues leaching into the soil and ground water from waste heap piles and abandoned mines.

The explosive compounds of primary interest are 2,4,6-trinitrotoluene (TNT), Royal Demolition Explosive (RDX) hexahydro-1,3,5-trinitro-1,3,5-triazine, and High Melting Explosive (HMX) octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine. Of the three, TNT contamination is the most prevalent due to its extensive use and manufacture during the past century. Related explosive precursors and daughter compounds include dinitrotoluene (DNT), trinitrobenzene (TNB), dinitrobenzene (DNB), and many other nitroaromatic and aliphatic compounds. These are used to manufacture not only explosives but also pharmaceuticals, pesticides, polyurethanes, foams, dyes, pigments, coatings, elastomers, and waterproofing agents (Roberts et al. 1986, Majors et al. 1994, Gorontzy et al. 1994)

POTENTIAL FOR DEGRADATION

Nitroaromatic compounds are xenobiotic (man-made) and highly recalcitrant. Xenobiotic compounds are not naturally occurring in the environment and therefore tend to resist natural decomposition processes. This makes them very difficult to remediate when they are released into the environment. Many of the nitroaromatic compounds and their daughter products exhibit toxic and mutagenic effects on life forms such as bacteria, fungi, yeast, unicellular algae, copepods, and oyster larvae (Won et al. 1974 and Nay et al. as reported by Marvin-Sikkema, 1994). Researchers have had difficulty demonstrating complete mineralization of explosives to carbon dioxide and water

under aerobic environments, or methane under anaerobic conditions.

TNT degradation has been shown to occur through two primary pathways. One, oxidation of the methyl group to form trinitrobenzene which can be degraded by sunlight, ozonation, and catalysis with the soil particles. Two, reduction of the nitro groups to form hydroxyamino and amino intermediates. Of the two pathways, the latter has been the observed preferential sequence (Majors et al. 1994, McCormick et al. 1976).

RESEARCH OBJECTIVES

The objective of this research was to implement a model that can be utilized as a predictive tool by environmental engineering professionals to assess the likely fate and transport of explosive compounds in the environment and to assist them in determining remediation alternatives for that particular site. The model incorporates physical, chemical, and environmental factors that directly affect the compound's rate of degradation and transport in the environment.

For the purposes of this thesis, a U.S. Army site known as the Umatilla Depot Activity (UMDA), near Hermiston, Oregon was used to illustrate the proposed model. The site of specific interest within the Depot was an explosives washout facility utilized to demilitarize conventional ordinance. The operation utilized a pressurized hot water system to extract (washout) the explosives from the bomb and shell casings. Wastewater from the washout facility was

impounded into an unlined lagoon system that allowed unrestricted percolation into the underlying soil, and ground water, and volatilization into the atmosphere (MKES et al. 1992).

CHAPTER 2.

LITERATURE REVIEW

To further understand the complexity of the problem, a brief discussion of how these compounds are manufactured and the prevailing chemical reaction mechanisms may provide insight as to why these compounds are so resistant to natural environmental degradation processes. A review of the available research and literature summarizes the controlling degradation systems for explosive compounds such as TNT, RDX, and HMX. Figure 2-1 illustrates the chemical structures of these three chemical compounds. To date, none of the cited research has been able to establish or determine degradation pathways of nitroaromatic compounds to complete mineralization. However, the research has identified some very important and critical partial degradation pathways of these very recalcitrant, xenobiotic compounds.

TNT MANUFACTURE

Trinitrotoluene (TNT) is the common name for 2,4,6-trinitrotoluene. TNT is formed when toluene is successively reacted with nitric acid (HNO₃) in the presence of sulfuric acid (H₂SO₄). Stoichiometrically, toluene releases hydrogen (H⁺) ions from its ring as the nitric acid releases hydroxide (OH) ions, thus allowing the nitro group(s) to attach to the unbalanced (charged) site on the ring structure. The nitration reaction of toluene to form trinitrotoluene requires 1 mole

$$O_2N$$
 O_2
 O_2N
 O_2
 O

Figure 2-1. Chemical Structure of TNT, RDX, & HMX.

of trinitrotoluene to react with 3 moles of nitric acid to produce 1 mole of TNT and 3 moles of water. Figure 2-2 describes the chemical equation reaction.

Toluene, which is a single methyl (CH₃) group attached to a benzene ring, is classified as an ortho-para directing group (Linstromberg et al. 1983). This means that during the addition of the first nitro group to the toluene ring there is a 70% preferential attachment at the *para* position rather than the *ortho* position. After the first nitro (NO₂) group is attached, the NO₂ group, which is a strong *meta* director, will dominate subsequent reaction mechanisms by placing the additional NO₂ groups *meta* to the original NO₂ group. Thus, successive nitration of the toluene ring directs the initial NO₂ group to the *para* position and the additional NO₂ groups *meta* from the NO₂ group. Successive nitration of the first two NO₂ groups is relatively straight forward. However, the addition of the third NO₂ group at the 6- position is more difficult because the two existing NO₂ groups have significantly reduced the overall activity of the compound.

This nitration reaction is 95% efficient in producing 2,4,6-TNT (α -TNT). The remaining 5% produces other unsymmetrical TNT isomers (Hao et al. 1991) such as 2,4,5-TNT or trinitrobenzene (TNB). Raw TNT must be purified to separate the impurities from the α -TNT. This is done by reacting the raw TNT with sulfite. The impurities react with the sulfite to produce sulfonated compounds that allow the α -TNT to be easily stripped away. The resulting sulfonated waste stream has a characteristic reddish color and is known as "red water."

Figure 2-2. Reaction Mechanism for the Production of TNT from Toluene.

TOXICOLOGY AND HEALTH EFFECTS

Compounds exist naturally in the environment in which we live. When these compounds adversely impact any species of life or cause an imbalance in the ecological stasis of the indigenous life forms, the compound is considered to be toxic to that environment. Toxic compounds may quickly disrupt the entire life cycle within that particular ecosystem or cause regional or global impacts. Thus understanding the toxic characteristics of individual and conglomerate compounds will help prevent negative insults to the environment, and assist in the restoration of negatively impacted ecological systems.

Toxicology.

Won et al. (1976) conducted mutagenic and toxicological studies on TNT and its intermediate metabolites. Won determined that TNT was very toxic to green alga, oyster larvae, and tidepool copepods and mutagenic to *salmonella typhimurium*. The initial reductive metabolites did not exhibit acute toxicity nor mutagenicity to the test populations.

Phillips et al. (1993) conducted soil toxicity studies using the earthworm as the test species. Three different ammunition plants provided various soil types, contamination levels, and contamination sources. Earthworms were hardier than Phillips' research team had anticipated. The worms gained weight in half the tests and survived all but one of the tests. Similar results were observed for the

RDX and HMX treatments. One test involving forest soils exhibited lethal effects at concentrations of 150 μ g/g. Earthworms were able to thrive in all of the other soils even at higher TNT concentrations (maximum of 500 μ g/g), but the forest soil exhibited inhibitory characteristics on the worms above the 150 μ g/g concentration. Philips offers that other soil constituents such as increased organic content and soil pH may contribute to this peculiar observation. The difference in organic content in the forest soils (5.9%) could be a primary factor over the other test soils organic content (1.4%).

Mammalian Toxicology

Shugart et al. (1991) conducted research at the Alabama ammunition plant to determine whether indigenous wildlife (deer, rabbits, and quail) were bioaccumulating explosive contaminants from ingesting surrounding water, soil, and plant life. Shugart referenced El-Hawari (1981) for determining the metabolites excreted from laboratory animals injected with TNT. Tissue samples were collected and did not indicate any TNT compound above 0.2 ppm nor was there any observed adverse affect on the wildlife. This led to the conclusion that the impacts on the wildlife would be minimal.

Roberts (1986) cites numerous researchers results. Specifically, laboratory animals have provided critical data not only in establishing their specific species response to acute doses of TNT but the data is also correlated to infer potential human response factors.

Health Effects.

Explosive compounds are one of the few industrial compounds that are well documented in terms of human response factors. This comes from the unfortunate exposures that were incurred during manufacturing operations.

Civilian and military munitions workers were exposed to compounds such as TNT, DNT, TNB, DNB, toluene, benzene, and other explosive precursors.

Roberts et al. (1986) compiled a comprehensive data summary on trinitrotoluene which summarizes significant research and reviews. Specifically, Roberts' report is comprehensive with detailed sections on toxicology, health effects and an extensive reference bibliography.

TNT has been shown to cause numerous effects on the liver, kidneys, heart, blood, pancreas, and central nervous system. Minor to moderate exposures result in significant hematological changes such as decreased blood counts in hemoglobin, red blood cells (RBC), and platelets; Heinz body formations; RBC dyscrasias; white blood cells changes (lymphocytosis and luekocytosis); and capillary fragility (causing nosebleeds and skin or membrane hemorrhages). Exposures at high concentrations may cause cyanosis or methemoglobinemia (RBC anemia). Chronic exposures in munitions (TNT) workers have experienced hemolytic anemia, cardiac effects such as dull heart beats, murmurs, EKG abnormalities, neurotoxicity, pancreatic toxicity, and nephrotoxicity (kidneys) which increases filtration rates and urination frequency.

Severe TNT exposures have caused death after the onset of acute effects including: yellow atrophy of the liver, aplastic anemia, bone marrow hypoplasia, and hepatoxicity of the blood. The list of ailments is quite lengthy. Listing the above health conditions demonstrates the effects that TNT exposure has on the various organs and tissues of the human body.

Roberts cites a few researchers', Jaffe et al. (1973), Rosenblatt et al. (1980), and Zakhari et al. (1978), reviews of acute exposure studies conducted on human "volunteers" during the 1940s. Exposure routes varied from oral, dermal (hands), and respiratory pathways. Past human "volunteer" and munitions workers documented health effects over a 60 year period (1917 through 1976) and provided invaluable data on human physiological responses to exposures from munitions compounds. Occupational exposure routes were generally from airborne vapors and dusts. Personnel normally exposed include munitions manufacturing personnel, munitions maintenance personnel, tunnelers, and miners.

Roberts' report (1986) indicates teratogenic (reproductive) effects have been reported (by Jaffe et al. 1973) to cause symptoms of irregular menstruation in female munitions workers resulting from chronic TNT intoxication. Male reproductive responses may be inferred from rat studies where testicular atrophy was questionably observed (by Dilley et al. 1978).

The data from human and animal exposures are critical factors in

establishing occupational and public health standards. Animal studies provide extrapolative evidence in determining lethal concentrations (LC₅₀) and lethal dosages (LD₅₀) of compounds such as TNT and other explosives. These standards are designed to minimize adverse effects to the public from chronic low dose exposures. Specifically, the EPA has adopted a protection scheme to assess whether "ambient" exposures are capable of causing at least one additional case of cancer in a population of one million people (1:1,000,000). These assessments can take the form of regulatory compliance (law) or strongly encouraged Health Advisories. The Department of Labor's Occupational Safety and Health Administration (OSHA) established occupational threshold limit values (TLVs) and maximum permissible exposure limits (PELs). TLVs provide regulatory guidelines on the maximum amount of contaminant that an individual can be safely exposed to without adverse health effects. The American Conference of Governmental Industrial Hygienists (ACGIH 1995) established TLVs of 0.5 ppm for TNT and 0.15 ppm for DNT. Both chemicals are annotated as being suspected human carcinogens. TLVs do not suggest that employers intentionally expose employees to chemical (or physical) hazards. The use of engineering controls, personal protective equipment, and chemical substitution are effective tools that employers are highly encouraged to utilize in order to minimize work related injuries and illnesses.

Health Advisories

In 1991, Roberts et al. established EPA Drinking Water Health Advisories (HA) for environmental contaminants specific to the U.S. Army. The EPA and U.S. Army entered into a memorandum of understanding to develop drinking water health advisories. An important aspect of health advisories are that they are not legally binding contamination levels even though they may be respected as such. Health advisories are calculated in a three step process by: a) determining the highest reference dose (RfD) which will not cause harmful health effects, b) establishing the drinking water exposure level (DWEL), and c) calculating the lifetime health advisory. Health advisories account for adult lifetime exposures, and one or ten day exposures for children. A child weighing 10 kilograms is assumed to drink 1 liter of water per day, while the average adult weighs 70 kg and consumes 2 liters of water per day. The reference dose is based on the maximum allowable concentration in which there is No Observable Adverse Effect Level (NOAEL) or the Lowest Observed Adverse Effect Level (LOAEL). The HA concentrations of four munitions compounds from Roberts' report are summarized in Table 2-1.

Explosive compounds are toxic to a wide variety of biological life forms that have been associated with traditional in situ remediation operations. Xenobiotic contaminants either impair the microbe or the microbes cannot consume the contaminant as a carbon source.

Table 2-1. Drinking Water Health Advisories (Roberts et. al. 1991)

		Concentration	(mg/l)	
Criteria	TNT	DNB	RDX	HMX
1 Day HA	0.02	0.04	0.10	5.00
10 Day HA	0.02	0.04	0.10	5.00
Long Term HA Child Adult	0.02 0.002	0.04 0.14	0.10 0.40	5.00 20.00
Lifetime HA	0.002	0.001	0.002	0.40
DWEL	0.02	0.005	0.10	2.00
EPA Cancer Group	С	D	С	D
NOAEL (mg/kg/day)		0.4	0.3	50
LOAEL (mg/kg/day)	0.5 (dogs)	1.14 (rats)	1.5 (rats)	115 (rats)
Uncertainty Factor	2		1	

The quest by the majority of the researchers has been to identify specific organism(s) that may be responsible for or capable of degrading the target compound. The focus of late has been centered around fungal systems and highly enriched cultures, identified from natural systems, that are capable of metabolizing the contaminant. Higher life orders, specifically mammals, have an ability to metabolize or excrete the contaminant. Mammals are not utilized as a viable remediation process.

DEGRADATION PATHWAYS

Determining the degradation reactions from laboratory research studies is the first step to understanding how the same reaction processes can be implemented under actual field conditions. Laboratory research provides degradation kinetics under controlled conditions that can be extrapolated to estimate the controlling parameters that affect full scale remediation. Modeling provides a predictive tool that can be used to evaluate, correlate, and calibrate the predictive parameters derived from the laboratory studies to full scale, field remediation processes. The following researchers have conducted critical laboratory research in their quest to degrade explosive compounds.

McCormick et al. (1976) first postulated that one of two reaction pathways may occur during the degradation of TNT: reduction of the NO₂ groups or oxidation of the methyl group. In the last ten years, the majority of the research has been to establish the degradation pathways of nitroaromatic compounds via

complete mineralization either aerobically or anaerobically producing carbon dioxide and water, or methane, respectively. Unfortunately, mineralization reactions have been difficult to determine and document.

Methyl Oxidation Pathway

Oxidation of the methyl (CH₃) group involves the sequential transformation to an alcohol (CH₂OH), aldehyde (CHO), carboxylic acid (COOH), and finally releasing CO₂ from the nitroaromatic ring. Trinitrobenzene is formed if the carboxylic acid group leaves the ring as carbon dioxide (Majors et al. 1994). Spanggord's (et al. 1980) study supported this reaction pathway because concentrations of trinitrobenzealdehyde, trinitrobenzoic acid, and TNB were observed during the study. Aerobic conditions in the top few inches of soil provide a desirable environment for methyl oxidation to take place. Figure 2-3 illustrates the oxidation of the methyl group through various transformation products.

Nitro Reduction Pathway

The majority of the research has focused on the reduction of the NO₂ groups. Additionally, NO₂ transformation products have been observed more often in natural environments than the methyl intermediates. NO₂ reduction involves the successive transformation of each NO₂ group to a hydroxylamino (NHOH) group and then to an amino (NH₂) group before the next NO₂ group is

Figure 2-3. Oxidation of TNT's Methyl Group.

reduced. Once all three NO₂ groups are converted, triaminotoluene (TAT) is formed. Triaminotoluene is very unstable and has been very difficult to measure analytically in the laboratory.

Reduction of NO₂ may also involve the dimerization of adjacent intermediately reduced TNT molecules to form azoxy-toluenes such as 2,2',4,4'-tetranitro-6,6'azoxytoluene or 2,2',6,6'-tetranitro-4,4'azoxytoluene (Won et al. 1974, Majors et al. 1994). This secondary pathway is also shown in Figure 2-4. The production of these dimers is more pronounced under aerobic environmental conditions. Researchers that observed the azoxy compounds noted no further degradation of them. Therefore, the production of azoxy intermediates is undesirable and should be minimized or altogether prevented.

The degradation of TNT via the NO₂ reduction pathway is preferred over the methylation or incomplete reductions that produce very recalcitrant dimers. Controlling the oxygen conditions is crucial to forcing the reaction sequence specific to the needs of the hazardous waste site. Soils near the water table are very low in free available oxygen, therefore, they tend to behave in an anaerobic fashion.

The production of the azoxy dimers can be attributed to whether aerobic conditions were encountered after initial anaerobic degradation conditions began. Inducing anaerobic treatments should be cost effective as lower volumes of materials are required to maintain an anaerobic versus aerobic environment.

Figure 2-4A. Successive Reduction of TNT's Nitro Group.

Figure 2-4B. Formation of Intermediate Azoxy Dimers.

Degradation Factors

Researchers have shown that the degradation of explosive compounds is a direct function of environmental, biological, physical, and chemical factors affecting the compound whether it resides as a contaminant in the soil or is in solution in an industrial waste stream. Environmental factors include soil geology, ground water depth and flow, and climatic conditions such as precipitation and evaporation rates. Biological factors focus on the ability of both indigenous and exogenous microbial and vegetative populations to utilize the contaminant as an energy or nutrient source.

As researchers systematically control these factors in their research, the information collected will eventually chip away the barriers preventing restoration of contamination sites or effective treatment of industrial waste waters. Many researchers have used TNT labeled with radioactive carbon (¹⁴C) in order to track the contaminant's fate as various environmental, biological, physical, and chemical factors are adjusted during the study.

Environmental Conditions

The environmental conditions placed on a contaminated site have a direct impact on the remediation processes that may or may not occur in the degradation of the contaminant. Under anaerobic conditions, the preferred degradation reaction is the reduction of the NO₂ groups to NH₃ groups. In

aerobic environments, the oxidation of the CH₃ group results in the formation of compounds such as trinitrobenzealdehyde, trinitrobenzoic acid, and TNB. It is speculated that azoxy compounds are formed when environmental factors uncontrollably change from anaerobic to aerobic conditions.

Biological Processes.

In the last twenty years, incremental advances have established specific fungal and bacterial populations capable of transforming explosives in laboratory environments. As researchers continue to understand the factors affecting these populations and the mechanisms involved, processes can be developed for full scale remedial implementation.

Fungal Processes.

The white rot fungus, *Phanerochaete chrysosporium*, has been receiving a lot of attention due to its ability to degrade xenobiotic, recalcitrant compounds. *P. chrysosporium* produces two unique extracellular enzymes; lignin peroxidase (LiP) and manganese peroxidase (MnP). These enzymes exhibit characteristics that enable it to degrade lignin and other recalcitrant compounds (Spiker et al. 1992). *P. chrysosporium* first received attention due to its ability to degrade wood and wood-preserving compounds such as creosote.

Fernando et al. (1990) grew white rot fungus in a matrix comprised mostly of corn cobs. The fungi-cob matrix was established to protect the fungi and

provide a stable growth environment. The matrix was mixed with TNT contaminated soils in hopes of degrading the TNT. They were moderately successful, 20% was metabolized to ¹⁴CO₂ and 50% was transformed to water-soluble daughter compounds. Fernando increased the TNT concentrations to field conditions of 10,000 ppm soil and 100 ppm liquid. The indications from this study imply that high concentrations of TNT were not inhibitory to the fungi.

Spiker et al. (1992) conducted another study and determined that *P. chrysosporium* were unable to tolerate TNT concentrations greater than 20 ppm. This study utilized soils from the Umatilla Depot in Oregon contaminated with concentrations of 12,000 ppm TNT, 3,000 ppm RDX, and 300 ppm HMX. Concerned that the combination of explosives and indigenous soils may be inhibitory to the fungus, pure TNT was also tested. It was determined that TNT was inhibitory at concentrations higher than 20 ppm. Spiker also varied the stage of the life cycle of *P. chrysosporium*. Both Fungal spores and established mycelial growth were introduced to the soils at various TNT concentrations. TNT transformation products were identified as "more water soluble" intermediates. These water soluble intermediates were likely hydroxylamino and azoxy daughter products. Spiker's results support the work done by Fernando et al. (1990). If the fungus can be protected and immobilized on a host matrix, it may be able to degrade higher concentrations of TNT.

Valli et al. (1992) degradation research of 2,4- Dintrotoluene by *P. chrysosporium* proposes specific degradation reaction pathways. Initial

degradation followed the NO₂ reduction pathway to form intermediates of 2,4-diaminotoluene, 4-amino-2-nitrotoluene, and 2-amino-4-nitrotoluene. The last compound was observed in the greatest concentrations and became the object of further study. Valli identified the second stage fungal metabolites as 4-nitrocatechol, 1,2-dimethyoxy-4-nitrobenzene, and 2,4-diaminotoluene. Additional degradation metabolites were also formed and are illustrated in Figures 2-5 and 2-6.

In the reaction pathways illustrated in Figure 2-6, both NO_2 groups are removed before the aromatic ring is fractured. After the reduction of one NO_2 group, the peroxidase oxidizes the contaminant to form an orthoquinone. Once this quinone is produced, the compound can then undergo a series of methylation and reduction cycles. Ultimately, DNT is transformed to 1,2,4-trihydroxybenzene and then to β -ketoadipic acid which is readily metabolized to CO_2 .

Bacterial Processes

McCormick et al. conducted several aerobic and anaerobic studies that identified several strains of *psuedomonas*, cell free *E. coli* enzymes (1976), and *Mucrosporium sp.* (1978) that were capable of transforming the NO₂ groups of TNT to NH₃ group intermediates. Cleavage of the aromatic ring was postulated to involve the further conversion of the NH₃ groups to phenols. The production of phenols was not observed nor was there evidence of ring cleavage. The

$$CH_3$$
 NO_2
 NO_2

Figure 2-5. Degradation Reaction of 2,4-DNT by P.chrysosporium. (Valli et al. 1991)

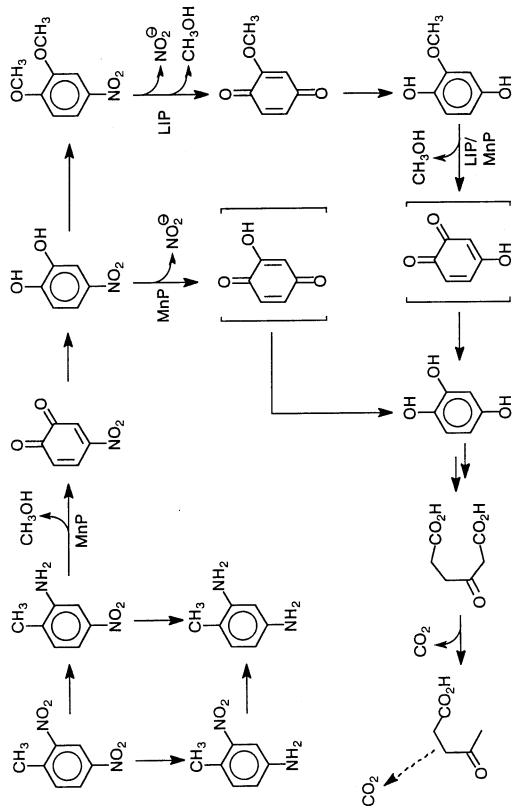


Figure 2-6. Proposed Mineralization of 2,4-DNT by P.chrysosporium. (Valli et al. 1991)

consortia were capable of reducing two of the three NO₂ groups to NH₃ groups as described previously by the NO₂ reduction pathway.

Bradley et al. (1994) investigated whether or not indigenous biological populations were responsible for degrading TNT from known surface contamination and causing TNT metabolites and daughter products to leach into the underlying aquifer and contaminate the ground water. Bradley used an inactive ammunition plant near Weldon Springs, Missouri to identify and confirm microbial activity and degradation products present in four different soil zones.

Bradley et al.(1994) concluded that the disappearance of the radio-labeled carbon (¹⁴C) test substrate was attributable to biological activity. Therefore, the ground water contamination was also the result of in situ biological activity. This study established that biodegradation is still possible in environments that inhibit fungal degradation processes. NO₂ group reduction was the preferred reaction observed during Bradley's study.

Bausum et al. (1992) conducted laboratory studies on river bottom sediments to identify microbial populations that may degrade DNT (both 2,4- and 2,6- isomers). Microorganisms obtained from waters downstream of the Radford, Virginia ammunition plant were capable of directly metabolizing DNT. Cultures of the mixed bacterial populations were enriched and were able to utilize DNT as the sole carbon source. 2,4-DNT degrading microbial strains were isolated but not identified in the report. The 2,4- isomer consistently disappeared or was

metabolized at a higher rate than the 2,6- isomer. In laboratory conditions this was more pronounced than in natural waters. Radio-labeling revealed that 60% was mineralized to CO₂. Bausum et al. (1992) suggests that since increased microbial populations were observed, a significant amount of the remaining ¹⁴C must have been utilized in the production of biomass. Microbial populations also responded as a function of the DNT concentration available. At concentrations above 0.1 mg/l, populations increased. At concentrations below 0.1 mg/l, there was no significant growth of the microbial population. Bacterial growth in the enriched cultures was approximated using first order kinetics. Reductions of 2,4-DNT and 2,6-DNT exhibited mean second order rates of 3.9x10⁻¹⁰ ml•cell⁻¹•min⁻¹ and 9.9x10⁻¹⁰ ml•cell⁻¹•min⁻¹ in the laboratory, respectively. Bausum et al. suggested the slower degradation rates for the 2,6-DNT isomer were attributed to the lag time required for the microbial population to initiate growth.

Boopathy et al. (1994a) identified a consortium of *Psuedomonas* able to utilize trinitrobenzene as its sole nitrogen source. The most active bacteria in the consortium were identified as *P. fluorescens* and *P. Mendocina*. Both are gram-negative rod species. Individually, the pseudomona did not significantly metabolize the trinitrobenzene. When the entire consortia of soil bacteria were used, enzymes were produced that metabolized the TNB. Boopathy speculates the degradation of TNB to dinitroaniline, which would be consistent with other observed pathways (Won et al. 1974; McCormick et al. 1976; Kaplan and Kaplan

1982). Boopathy et al. (1994a) further suggests that the dinitroaniline is deaminated to form dinitrobenzene. Dinitrobenzene can be reduced again to form nitrobenzene. Nitrobenzene was observed as an end product accumulating in the culture medium during the study. An important aspect of this *Psuedomonas* consortium is that it was using the contaminant, trinitrobenzene, as a nitrogen source, leaving the aromatic ring intact, and releasing ammonia into the culture. This contrasts previous research because the release of nitrite had not been observed.

In a different study, Boopathy et al. (1994b) observed that a newly discovered methanogenic bacteria, *Methanococcus sp.* (strain B) transformed several nitroaromatic compounds. Boopathy and Kulpa (1993) isolated this specific bacterium from lake sediments. The bacteria was able to degrade the compounds: TNB, DNB, NB, 2,4-DNT, 2,6-DNT and 2,4-dintrophenol. The bacteria reduced the contaminants co-metabolically when a primary electron donor and nitrogen source were supplied. Sulfide levels of 0.05 mM provided sufficient nutrients for all the methanogens studied. NO₂ reduction to NH₃ group end products was observed. In this report, Boopathy (1994b) cited a previous study (Boopathy and Kulpa 1993) in which *Desulfovibrio* sp. (B strain) reduced TNT to triaminotoluene (TAT). Triaminotoluene is very unstable and is quickly deaminated to toluene. This is important because remediation mechanisms for benzene and toluene are well known and not further discussed.

Funk et al. (1993) utilized an anaerobic procedure that has remediated soils contaminated with the nitroaromatic herbicide dinoseb (2-sec-butyl-4,6dinitrophenol). Soil cultures were prepared from a soil inoculum obtained from a dinoseb-contaminated site in Ellensburg, Washington. The cultures contained aerobic heterotrophs capable of growing with respiratory inhibitors (TNT and dinoseb) and anaerobic organisms capable of degrading the dinoseb. Funk used TNT contaminated soils from the Umatilla Army Depot, Oregon. Indigenous bacteria were fed potato starch in order to induce anaerobic conditions in the soil cultures. The cultures degraded the explosive contaminants by transforming one of the NO₂ groups to an NH₃ group. Optimum anaerobic conditions were determined by varying the temperature and pH. Temperature ranges of 20°C to 37°C and pH ranges of 6.5 to 7 were cited as optimal. Elevated pH (anaerobic) conditions resulted in the formation of undesirable azoxy-dimers. Initial supplements of ammonium chloride were beneficial, as Funk noted that explosive contaminated soils are often nitrogen deficient or limited. As degradation occurs, the nitrogen demand lessens as ammonium is released from the hydroxylaromatic intermediates and is available to the cells.

Biological systems are a primary focus of the research community for remediating hazardous waste sites. Because biological systems are living organisms, their substance, growth, and decay, depends on a complex interaction between the climatic and ecological conditions to which they are

exposed. For instance, northern climates may require longer remediation times as most organisms go into a dormant state during low temperature conditions.

Also, because of the extensive research already conducted, many of the studies are being validated or refuted by other researchers as they try to implement or expand on previous works. Therefore, the timeliness of the research is very important as incremental advances are continuously being made. For instance, Funk et al. (1993) disputes Fernando et al. (1990) research that *P. chrysosporium* is capable of concurrently degrading both TNT at 12,000 ppm and RDX at 3,000 ppm at these concentrations. Funk's research, which confirms Spiker et al. (1992), indicates that concentrations above 0.02% wt/vol (200 ppm) significantly inhibit the degradation of TNT.

As researchers strive to definitively determine the reaction mechanisms and the supporting factors that will completely mineralize explosive compounds, their interest and enthusiasm is rekindled from the detection of small amounts of ¹⁴CO₂. This is significant in that there must be a mechanism occurring that is mineralizing the contaminant to this elemental compound. Although the presence of the radio labeled carbon dioxide (¹⁴CO₂) is promising, none of the literature reviewed identifies specific mechanisms that could be expanded upon and incorporated into a pilot or full-scale remediation system.

Finally, the ecological environment in which the biological populations inhabit requires that sufficient supporting factors do not become rate limiting.

While hoping that the contaminant will be utilized as the primary energy (carbon) source, other factors such as the amount of available electron acceptors and donors (oxygen and hydrogen), nutrients (such as phosphorus, nitrogen, & sulfur) must also be tracked and accounted for. Soils and sediments that contain less than 5 to 10% aerated pore spaces tend to exhibit microbial activity characteristic of anaerobic environments. This is primarily due to the low oxygen diffusion coefficient of the ground water (Bradley 1994).

In situ biological systems often demonstrate higher degradation efficiencies when indigenous populations are properly motivated to metabolize the contaminant in contrast to the introduction of an externally adapted bacterial consortium that may have difficulty just being adequately delivered to the contamination zone. The discovery of indigenous populations in freshwater systems downstream from an AAP near Radford, Virginia and soils from a fertilizer facility in Washington capable of at least partial degradation, indicate that organism adaptation is possible (Bausum et al. 1992 and Funk et al. 1993).

Vegetative Processes

Vegetative processes are gaining strong favor due to a variety of remediation benefits. These benefits include increased depth of contaminant removal primarily due to root water uptake. Vegetation also increases the organic content of the soil. The root system and the increased organic content of the soil provide additional adsorption sites to which the contaminants can attach.

Finally, establishing vegetative cover minimizes contaminant dispersion and migration due to soil erosion by wind and water.

Banwart et al. (1991) determined the recovery effects of various plant species when treating TNT soils with the addition of organic residue amendments. When amendments were added to the contaminated soils, plants coped better against the contaminant-induced stresses. Rye grass demonstrated the most tolerance to the TNT compounds as it was almost indifferent to the percentage of amendments. All three plant groups, sorghum / Sudan grass mixture, alfalfa, and perennial rye grass, responded well to any combination of amended soils greater than 10%. Once the TNT was adsorbed, Banwart's analytical methods could not identify the fate of the compounds; either by removing or detecting them in the soil matrix or the plants' tissues.

Mueller et al. (1992) studied whether plant cells adsorbed, internalized, transformed, or metabolized the TNT contaminants. Initial results indicated that the cells did in fact internalize and convert the TNT into intermediate products described previously. Secondarily, Jimson weed, *Datura innoxia and Datura quercofolia*, and a wild tomato plant species, *Lycopersion peruvianum*, were transplanted into known concentrations (500, 750, and 1,000 ppm) of TNT contaminated soils. After two weeks, the plants were removed and the concentrations of carbon labeled (¹⁴C) TNT intermediates were measured in the roots, shoots, and leaves. Root concentrations of degradation compounds were

as high as ten times (10x) that of the contaminated soil, while the amount of the raw TNT in the root was less than 10% of the total. Concentrations in the above ground plant sections were detected but not further enumerated. The Jimson weed, *D. innoxia*, tolerated concentrations of 1,000 ppm without exhibiting contaminant-induced stresses. Mueller believed that if the duration of the study were continued, more contaminant would have been translocated into the upper parts of the plant.

Skogerboe et al. (1991) conducted a study of surface runoff, and plant growth and bioaccumulation tests on an explosive ordinance site at a U.S. Navy submarine base in Washington. The establishment of vegetative covers on bare, TNT contaminated soils reduced suspended solids from 1,000 mg/l to 10 to 20 mg/l. Soil TNT concentrations tested were 3.3 mg/kg, 30 mg/kg, and 3,030 mg/kg TNT. Skogerboe established tall fescue on all the soils except the samples with the highest concentration.

The addition of soil amendments (horse manure) increases the plant's tolerance to the TNT. Good plant growth was observed at concentrations up to 900 mg/kg. Plant uptake determinations were not conducted due to poor recovery methods from plant tissues. Concentrations greater than 100 mg/kg severely inhibited the growth of tall fescue and may require soil amendments. Localized hot spots could be tilled to reduce the average concentration in order to establish grass cover. Finally, vegetative covers should utilize low preference

grazing plant species. This may discourage wildlife from grazing within the remediation zone. If this is not feasible, the use of high preference grazing vegetation should be planted elsewhere to attract them away from the area (Skogerboe et al. 1991).

Pennington et al. (1989) conducted a study that was unable to attribute any significant remedial degradation of explosives due to plant uptake. Pennington studied the contaminants TNT, 4ADNT, and 2ADNT from two soils, Sharkey clay and Tunica silt with the test plant yellow nutsedge. Contaminant concentrations were applied at 80 μ g/g of soil. Varying the pH at any of the treatment levels did not significantly increase plant uptake into the plant's leafy portions.

Pennington's study may only be able to suggest that clay and silty materials may not release the explosive from the soil matrix into the plant's structure. Harvesting of root material was not reported so as to determine the effect of adsorption from the soil matrix to the root structure nor were the roots tested for concentrations of explosives. This can be attributed to a couple of factors. One, the increased number of adsorption sites provided by the clean amendments and, two, the dilution factor of adding non-contaminated materials to the soil (Banwart et al. 1991).

Vegetative remediation processes offer a variety of benefits that make it attractive to explosive contaminated soils. The majority of explosive

contamination is surface contamination. Surface concentrations are typically an order of magnitude higher than deeper soil and ground water contamination levels. Once the vegetative population is established, the roots not only provide adsorption sites but also provide a contaminant sink which draws the explosive from the soil-water pore spaces. Previous research by Mueller did not identify the degradation compounds present in each of the plant sections. Additionally, research has not determined whether breakdown occurs as a result photosynthetic processes. These questions illustrate the need for additional research that addresses these issues in a manner that permits engineers and remediation specialists to use the information productively.

Ex Situ Biological Processes

Composting. Composting is the only bioremediation process that has been tested in field-scale conditions. Currently, the U.S. Army is composting explosive contaminated soils at many of its ammunition plants. Composting is effective at reducing original TNT concentrations to oxidative and reductive intermediates, but has yet to demonstrate permanent binding of the intermediates within the soil-compost matrix. If this cannot be demonstrated, disposal as hazardous waste may be the ultimate result. This would be less economical than initial hazardous waste disposal due to the increased volume from the added compost ingredients (Williams et al. 1989, Griest et al. 1991, Majors et al. 1994, and

Kaplan and Kaplan et al. 1982).

Humification. Humification is a process that transforms compounds such as aromatics to naturally occurring humic and fulvic acids in the soil. Majors et al. (1994) postulates that this process may be likely if the soil environments are alternately rotated between anaerobic and aerobic conditions several times. This alternating oxidative environment may be able to provide the formation of imine bonds and secondary amine bonds.

A differing reaction process, that may achieve similar results is the reaction of the aromatic amine and quinones resulting in the formation of secondary amine bonds (Parris, 1980 as reported by Majors et al., 1994).

Soil Slurry Reactor. Manning et al. (1991) utilized a soil slurry reactor to reduce TNT concentration levels by about 90%. Aerobic and anoxic reactor configurations were alternated in order to reduce contaminant concentrations cometabolically. No further discussion or explanation of the mechanics or kinetics of the system were presented.

Physical / Chemical Processes

There are many physical / chemical processes that may be capable of treating waste streams and degrading contamination from explosives production, maintenance, and disposal operations. The majority are traditional treatment processes utilized for municipal and hazardous waste treatment. These include,

carbon adsorption, destruction by light (photolysis), composting, wet air oxidation, and incineration.

Photolysis. The most prominent natural physical / chemical process that degrades TNT is photolysis. Photolysis is the result of exposure to ultraviolet light or sunlight. Photolytic degradation is significant in the top few inches of contaminated soils and waste waters (Roberts, 1986). Formation of azoxy diisomers, 2,2',6,6'-tetranitro-4,4'azoxytoluene or 2,2',4,4'-tetranitro-6,6'azoxytoluene, from the coupling of hydroxylamino and nitroso intermediates were observed (Spanggord et al. 1981, 1983). These di-isomers are dead end products that are much more resistant to further degradation than the nitro reduction or methylation intermediates.

Although hard to control, photolytic processes should be minimized to prevent excessive production of these recalcitrant di-isomers. These di-isomers may provide a contaminant reserve that slowly releases leachate affecting the ground water below.

Granular Activated Carbon. Freeman (1991) suggested that the only effective means of treating explosive manufacturing waste waters (Red Water) is the use of granular activated carbon (GAC). The high regeneration and disposal costs are GACs main problems. Regeneration facilities might have a problem of high reactivity while trying to regenerate the spent GAC. Therefore, disposal of spent

GAC as a hazardous waste is necessary. This has made explosive production very costly. In fact, the U.S. Army halted production of the explosives TNT, RDX, and HMX until an effective treatment method can be implemented to adequately dispose of red water waste streams (Freeman (1991), Hao et al. (1991), Majors et al. (1994), and Gorontzy et al. (1994)).

Wet Air Oxidation (WAO). Freeman (1991) and Hao et al. (1991) both suggest alternative processes, such as wet air oxidation, for effective treatment of TNT red waters. WAO is ideal, over incineration, for wastes with low solids (high liquids faction) content. WAO is a treatment process that utilizes high temperature, high pressures, and supplemental oxygen to break down the waste. Theoretically, WAO end products are CO₂, water, nitrogen (or ammonia), and solids converted to their highest oxidative state.

Freeman further suggested incorporating powdered activated carbon (PAC) sludge treatment (PACT) with the wet air oxidation process. One of the major benefits of coupling the two technologies is that the PAC can be regenerated locally by the WAO process. Major disadvantages of the PACT / WAO system are the high costs associated with procuring and maintaining the equipment.

Incineration. Incineration is the ultimate destruction process in regards to hazardous waste. Incineration is not only expensive but negative public

connotations are always associated with it. Public concern aside, the total costs of incinerating explosive contaminated ammunition plant soils may be as high as \$1.5 billion. Normal costs are approximately \$300 to \$600 per ton for quantities less than 20,000 tons and \$200 to \$300 per ton for larger volumes (Williams et al. 1991).

All the physical and chemical processes ex situ techniques require physical removal of the contaminated soil or soil-water and processing it through a mechanical system. The main disadvantage is the very high cost associated with these systems.

On a final note, in support of incineration, it is the only process that is capable of breaking the contaminant down to elemental components. A slight drawback is that it also renders the waste (ash or soil) material virtually inert and sterile. Sterile soils are not desirable when restoring a site. Vegetation and biological systems are very difficult to reestablish in sterile soil matrices.

Therefore, additional capital is required to augment the soil with natural amendments or other soil mixing techniques when restoration or replacement is desired.

SUMMARY

It is important to note that none of the cited research established a degradation step linking the removal of the nitro or amino groups from the

original compound. In other words, TNT has not been shown to degrade directly to DNT. Degradation experiments that recovered radio-labeled carbon dioxide could not establish a documented pathway to explain the cleavage of TNT's ring to elemental compounds.

The use of indigenous microbial populations has shown the most promise in remediating other hazardous waste sites. These same populations may require acclimation or a primary substrate source to serve as an electron donor or energy source in order for the microbes to at least co-metabolize the contaminant to elemental products or at least non-hazardous intermediates. Vegetative systems offer the additional benefit of minimizing the downward leaching of the contaminant into underlying aquifers and uncontaminated soils. They may also be capable of reversing the leaching effects due to the plant root's ability to attract, internalize, uptake, and possibly transform the contaminant.

CHAPTER 3.

DEVELOPMENT OF THE MODEL

Today, in situ remediation methods are the most desirable choice in remediating hazardous waste sites over traditional methods of ex situ processes of the last 25 years. Ex situ processes are well known for their overwhelming capital requirements and manpower intensity. Colossal efforts and high costs associated with excavation, transportation, and disposal operations were often the "norm." In situ processes, on the other hand, exploit natural processes and often enhance indigenous biological systems to detoxify the antagonistic hazardous compound. In situ processes, when viable, are often more efficient and effective at reclaiming the contaminated area to a useful purpose.

One common problem associated with in situ remediation is that it is very difficult to visibly confirm that degradation is occurring. Through the use of monitoring systems, real time sensors, and analytical models, in situ remediation can demonstrate remedial restoration without visible on-site excavation and disposal operations.

Remediation models are used for two very distinct reasons. The first is to demonstrate the expected results of all the various alternative remediative processes hypothesized during the Remedial Investigation / Feasibility Study (RI/FS) process. The RI/FS model should predict and provide an understanding

of the fate and transport of the target contaminants through the affected soils and water (surface and ground) systems and identify critical environmental and holistic community resources at risk. The second is to integrate the theoretical and scientific concepts with data obtained from the field. This integration results in real time monitoring of the in situ reactor and tracking the progress of the remediation project. In situ systems are difficult to monitor because the reactor vessel has many unknown variables that are often assumed because they are difficult to define. Maintaining sufficient balance of electron acceptors, nutrients, and moisture within the in situ reactor can be a challenge. Each in situ reactor has unique characteristics that require competent process knowledge of the physical, chemical, and biological mechanisms involved. Otherwise, ineffective treatment will occur that may prevent further in situ processes from being reinitiated.

DEVELOPMENT AND DESCRIPTION

This thesis will utilize the model, BIOROOT, to monitor the fate and transport effects of TNT contamination at the Umatilla Depot in northern Oregon. BIOROOT has been used to model the transport of a conservative contaminant in two dimensions through a variably saturated soil (Tracy et. al. 1992, 1994). The model solves a series of second order partial differential equations using a Galerkin finite element solution technique that employs quadratic isoparametric elements and a Crank-Nicolson difference method for the time derivative

interval. BIOROOT assumes the target contaminants will be transported through a porous media following an advective-dispersive behavior. The model assumes that the adsorption capacity of the soil behaves linearly and is a function of the bulk density of the soil. The contaminants are also assumed to be influenced from biological effects including microbial populations and vegetative processes. However, if limited contaminant degradation information is available, the degradation can be simulated as a first order decay process.

Specific parameters relating to the soil, plant, and microbial species should be obtained from either laboratory experiments, field surveys, or estimated from known reference data through a variety of methods (Zappi et. al. 1991, Lyman et. al. 1982, Howard et. al. 1991.)

The governing mass balance equation for the fate of a contaminant in BIOROOT is shown below:

$$\frac{\partial}{\partial x} \left[\theta \left(D_{xx} \frac{\partial C}{\partial x} + D_{xz} \frac{\partial C}{\partial z} \right) - V_{x} C \right] + \frac{\partial}{\partial z} \left[\theta \left(D_{zx} \frac{\partial C}{\partial x} + D_{zz} \frac{\partial C}{\partial z} \right) - V_{z} C \right] - (q T_{scf} + k) C =$$

$$\underline{\partial \left[C \left(\theta + R_{d} R_{cf} + \rho_{b} k_{1} \right) \right]} \partial t$$
(1)

Where:

1 . . .

θ soil-water content

 ρ_b bulk density of the soil

C solute concentration

D Dispersion coefficient

k first order decay rate

k₁ adsorption coefficient

K, hydraulic conductivity of the root

K_s hydraulic conductivity of the soil

g soil-water extraction rate by the plant's root system

R_d density of the root mass in the soil volume

R_{cf} root concentration factor

t time

T_{scf} plant's transpiration stream concentration factor

V Darcy soil-water flux

x horizontal spatial dimension

z vertical spatial dimension

The dispersive-advective effects (θDii∂C/∂i and ViC, respectively) are represented by the partial differentials in the horizontal (x) and vertical (z) dimensions. The contaminant sink (-qTscfC) from the plant's uptake of the contaminant and the rate of contaminant decay (-kC) complete the mass balance of the contaminant entering and leaving the control volume.

The right hand side of the equation expresses the change in the mass balance of the contaminant within the soil control volume with respect to the temporal dimension. The total contaminant mass flux is equivalent to the change in concentration within the soil-water (C θ), the amount sorped onto the root structure (CR_dR_{cf}), and that sorped onto the soil particle ($\rho_b k_1 C$). The model also assumes that linear isotherm adsorption models adequately simulate the contaminants adsorption (k_1) to the soil particles.

ADDITIONAL RELATIONSHIPS

Plants have an ability to adsorb and transfer hazardous organic compounds into its transpiration stream. The contaminant concentration in the transpiration stream (C_{ts}) is a direct function of the plant's transpiration

concentration factor (T_{scf}) and the solute concentration (C) as shown (Tracy et al. 1994).

$$C_{ts} = T_{scf}C \tag{2}$$

 T_{scf} is, in turn, a function of the contaminant's octanol-water partition coefficient, K_{ow} (Briggs et al. 1982).

$$T_{scf} = 0.784e^{\left(\frac{-(\log K_{ow} - 1.78)^2}{2.44}\right)}$$
 (3)

The root system not only provides additional adsorption sites onto the root structure itself but is also responsible for removing the contaminants from the soil matrix and transporting the contaminants into the plant's upper stem and leaf structure. Therefore, the plant provides a sink (S) for the contaminant. The contaminant sink is a function of the plants' intake of the contaminated soil-water flux (q) and the root transpiration stream concentration (Cts) from equation 2. Rewriting equation 2 yields:

$$S = -qT_{sef}C \tag{4}$$

The adsorbed concentration (C_r) onto the root structure is the product of the root concentration factor (R_{cf}) and the solute concentration:

$$C_{r} = R_{cf}C \tag{5}$$

Again the root concentration factor demonstrates a functional relationship with octanol-water partition coefficient (Briggs et al. 1982).

$$R_{\rm ef} = 0.82 + 10^{(0.77\log K_{\rm ow} - 1.52)}$$
 (6)

The model also assumes that the soil-water content is a function of the soil-water pressure head (Brutsaert, 1966).

$$\theta = \eta \frac{A}{A + \left(-\psi\right)^{c}} \tag{7}$$

Where:

η soil porosity

 ψ soil water pressure head

A.c soil characteristic parameters

The soil hydraulic conductivity is a function of the soil-water content (θ) and the term d, which is another soil characteristic (Brooks and Corey, 1966)

$$K_{s} = K_{sat} \left(\frac{\theta}{\eta}\right)^{d} \tag{8}$$

Where:

K_s effective hydraulic conductivity of the soil

K_{sat} saturated hydraulic conductivity of the soil.

Equations 9 and 10 apply the distribution of the soil-water pressure head using Darcy's law to determine the water flux in the vertical and horizontal components as:

$$V_{x} = -K_{s_{x}} \frac{\partial \psi_{s}}{\partial x} \tag{9}$$

$$V_z = -K_{s_z} \frac{\partial (\psi_s + z)}{\partial z}$$
 (10)

Where:

 ψ_s soil water pressure head

 V_x Darcy soil-water flux in the x dimension

CHAPTER 4.

SITE CHARACTERIZATION

A hazardous waste site near Hermiston, Oregon was chosen as the site to demonstrate the BIOROOT model's ability to simulate the fate and transport of the contaminant through the soil and groundwater. Normal environmental conditions with various remediation technologies is compared to a "No Action" alternative of the remediation process. The site is a U.S. Army munitions facility known as the Umatilla Depot Activity (UMDA). UMDA is a US Army facility being closed under the Department of Defense's Base Realignment and Closure Program and has been the focus of numerous environmental remediation investigations and feasibility studies to determine the extent of the environmental cleanup required to return the facility and associated land to the public and private enterprise.

Characterization information and parameters particular to this site were obtained from technical reports prepared by Dames and Moore (1994) and Morrison Knudsen Environmental Services and CH2M Hill (MKES et al. 1992) for the US Army Corps of Engineers Toxic and Hazardous Materials Agency.

SITE BACKGROUND.

The UMDA complex had an explosives washout facility that was operational for 15 years from 1950 to 1965. Washout operations are best

described as a hot wash water and steam cleaning system that removed the explosive compounds from the various munitions' components. On a weekly average 150,000 gallons of wash water were discharged to a lagoon system (See Figure 4-1). Ultimately, estimates of approximately 85 million gallons of explosive wash water had been impounded in the lagoons.

SITE LOCATION AND DESCRIPTION.

UMDA is located in the upper northeastern region of the state, located three miles south of the Columbia River. The Columbia River provides a portion of the north-south border with the state of Washington. The city of Hermiston, Oregon is located east of the depot. The washout lagoons are located in the central portion of the UMDA complex. The lagoons are located in a general area of a depression that slopes northeasterly toward the Umatilla River. The original lagoon system consisted of two lagoons each being 80 feet long with the north lagoon being 39 feet wide and the south lagoon being 27 feet wide. Typical depths average 6 feet. The lagoons were constructed with gravel side and central berms and sandy bottoms. The berms are 15 feet wide at the top and have side slopes of 35°.

CLIMATE.

The climate for this region has been identified as a cold, semi-arid desert.

Annual precipitation averages 8 to 9 inches, while evaporation averages 32

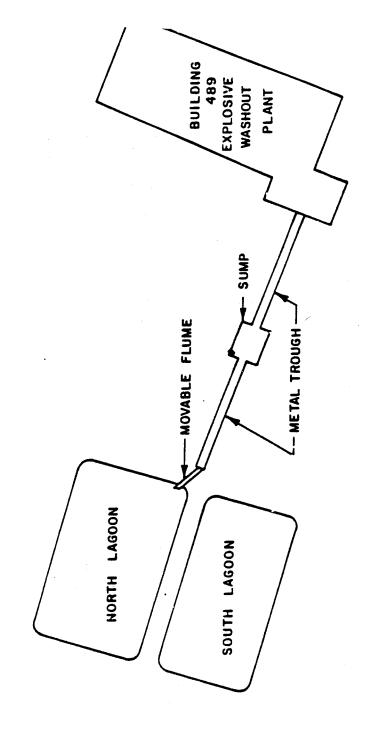


Figure 4-1. Explosives Washout Lagoon, Umatilla Depot Activity, Oregon (MKES et al. 1991)

inches. Vegetative species typically consist of arid grasses and shrubs.

Temperatures range from -31°F to a maximum of 113°F. Average summer temperature is 75°F while the average winter temperature is 35°F (MKES et al. 1992).

GEOLOGY.

The underlying soils are glaciofluvial flood sediments, which are highly permeable. Surface drainage is poorly developed due to the ground surface's high permeability. The soils beneath UMDA are predominately from two major geologic formations. The upper soil formations are a glacial flood gravel and the underlying bedrock formation is known as the Columbia River Basalt formation. The glacial flood gravels range in thickness up to 200 feet and thin out at the slopes of the valley. Figure 4-2 illustrates the geologic profile of the greater Umatilla area (MKES et al. 1991). The Umatilla Depot is located on a thicker region of the flood gravel deposit. The flood gravel deposit forms an unconfined aquifer with a saturated thickness of at least 40 feet in the vicinity of the lagoons. Depth to the unconfined aquifer has been measured from 40 to 50 feet below the ground surface. The thickness of the basalt formation was not reported. However, the southeastern corner of UMDA contains the highest elevation of the formation at 490 feet. The basalt has a general slope toward the northwest.

Finally, the confined aquifers beneath UMDA are formations comprised of interbeds between unweathered basalt flows. The upper system is the Selah

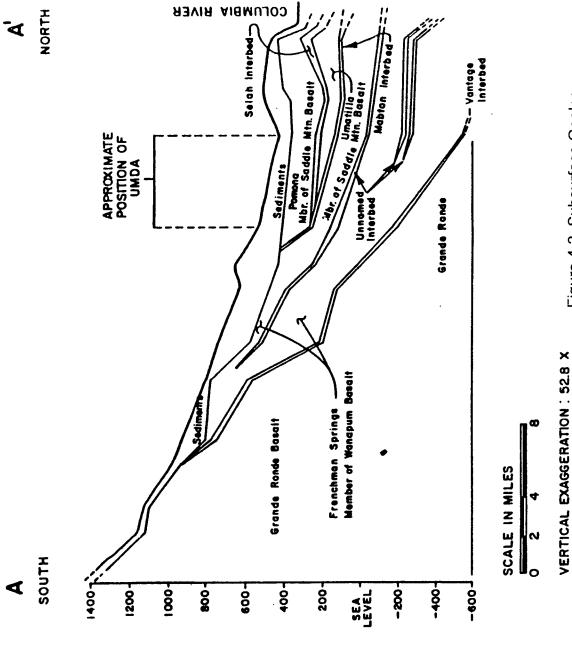


Figure 4-2. Subsurface Geology Morrow County, Oregon (MKES et al. 1991)

Interbed and the upper confining layer is identified as the Pomona Member of the Saddle Mountain Basalt formation which consists of weathered and unweathered basalt. It is generally believed that the confined aquifers are recharged from the higher sloped regions. None of the cited references (within MKES et al. 1992) suspected or identified that any of the confined aquifer systems were contaminated from the washout lagoons.

The direction and magnitude of flow from any of the ground water sources were not specified. Discharge to the Columbia River is likely and discharge from natural springs along the Umatilla River suggest natural ground water flows to be north by northeasterly toward one of the two river systems. Ground water pumping is suspected of controlling and reversing the ground water's flow as explosives contamination now appears to be migrating south by southeast. No specific reason was mentioned for this pumping whether it be for drinking water or for remediation purposes.

CONTAMINATION PRESENT.

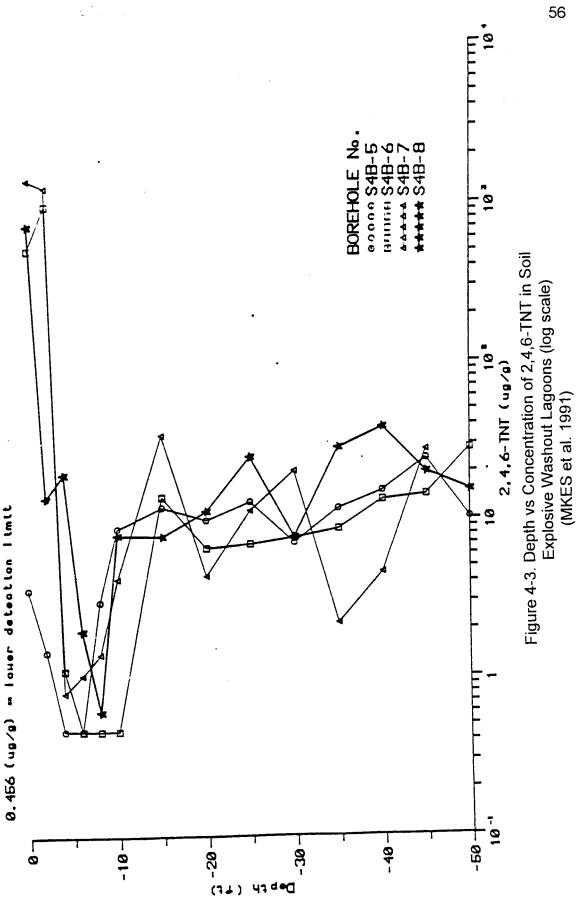
Previous supporting work (Weston, Ana-Lab Corporation, Century Environmental, Batelle, and Dames & Moore reported by MKES et al. 1992) identified the major contaminants as 2,4,6-TNT, 2,4-DNT, 1,3,5-TNB, HMX, RDX, nitrate and nitrite contamination. Explosive compounds were detected in the soil surrounding and beneath the lagoons. In addition to the explosives, nitrates and nitrites were detected only in the ground water. The greatest

concentrations of TNT were measured in the first 2 feet below the ground surface and ranged from 520 to 1,400 μ g/g. Localized "hot spots" were as high as 38,000 μ g/g but were generally less than 9,000 μ g/g. Detected levels of TNT decreased significantly from 1,400 μ g/g to as low as 1 μ g/g at depths of 10 to 12 feet. Depths greater than 12 feet exhibited concentrations not exceeding 50 μ g/g down to the water table (~50 feet). Figures 4-3 and 4-4 plot the depth of TNT concentration inside the lagoons from boreholes that cross-sectioned the lagoon system.

SOIL CHARACTERISTICS.

General soil characteristics for the first ten foot depth in the explosive washout lagoon area are summarized in Table 4-1. The soil parameters reported are: alkalinity, pH, moisture content, and total organic carbon (MKES,1992). The pH range, 7.6 - 8.4, was very tight, while the moisture content ranged from 3.5% to 17.5%.







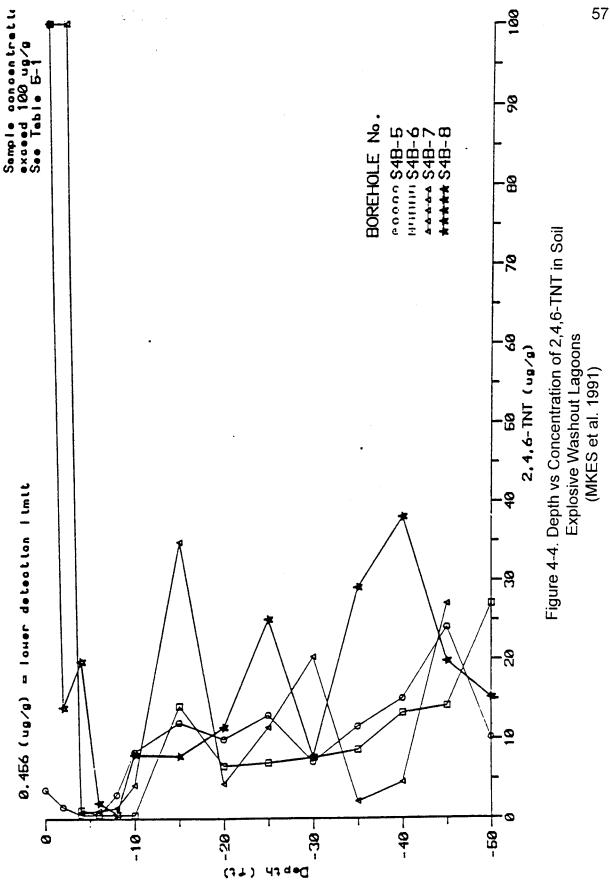


TABLE 4-1. SHALLOW SOIL CHARACTERISTICS FOR
UMATILLA EXPLOSIVE WASHOUT LAGOONS
(DAMES & MOORE, 1991)

SITE ID	DEPTH (feet)	ALKALINITY ^A (μg/g)	PH	Moisture Content (%)	TOC (g/kg)
	0	<25	7.64	4.7	0.892
S4B-5	4	48	8.19	4.8	3.33
	10	52	8.11	7.1	0.808
	0	102	8.27	5.2	7.34
S4B-6	4	46	8.19	5.4	3.6
	10	50	8.11	16.7	1.42
	0	194	8.35	5.3	4.88
S4B-7	4	50	7.87	17.5	3.12
	10	66	8.08	6.6	2.19
	0	54	8.2	3.5	1.93
S4B-8	4	50	8.4	5.4	1.18
	10	194	8.3	4.7	0.841

Alkalinity = Total Carbonate alkalinity (μg/g).

CHAPTER 5.

MODEL PARAMETERS

The BIOROOT model utilizes a finite element method for estimating the fate and transport of a contaminant through the soil profile. This requires developing a grid system that breaks down the soil profile into specific regions that mass balance relationships can be applied. The model also requires that specific soil parameters be known or estimated.

SPATIAL DEVELOPMENT OF FINITE ELEMENT MODEL.

The two lagoons of the explosives washout facility represent an area of roughly 6400 feet square within the berms. Soil samples indicate that there are areas of significant contamination outside the bermed area.

The RI/FS reports indicate the soil's contaminant concentration profile has the highest measured values in the first two feet. Contaminant concentrations decrease significantly within in the top ten feet and return to a nominal concentration within the seasonal variations of the water table. Just above the water table it is believed that the water table behaves like a contaminant source to the immediately overlying soil formations (MKES et al. 1991).

The finite element method utilized by BIOROOT incorporates a spatial grid that has three horizontal nodes spaced within one meter. The horizontal dimensioning will permit the evaluation of the site based on a elemental unit

area equivalent to 1 square meter. The vertical orientation subdivides the first meter in quarters, the next two meters are divided into ½ meter increments, and the remaining depth is divided at an even 2 meter distribution to a total depth of 25 meters (approximately 80 feet). The water table was reported to be approximately 15 meters (50 feet) below the ground surface. Figure 5-1 illustrates the fundamental vertical spacing of the elements implemented for this study.

This elemental and nodal representation of the UMDA washout facility demonstrates the ability of the BIOROOT model in simulating the contaminant transport through the zone of interest. The hydraulic conductivity reported for the UMDA soils vary considerably between the various consultants. MKES et al. (1991) reported values approaching 277.44 feet per day (84.6 m/day) and the District Corps of Engineers (1992) reported values up to 3247 feet per day. These values are indicative of clean sands and gravels (Freeze and Cherry, 1979).

BOUNDARY CONDITIONS.

The boundary conditions affecting the finite element model are the initial known heads of the unconfined aquifer. The magnitude and direction of the ground water flow were not cited sufficiently in any of the literature to incorporate realistic assumptions into the model. Therefore, the precipitation and evaporation data represent the only sources of known water fluxes in the model.

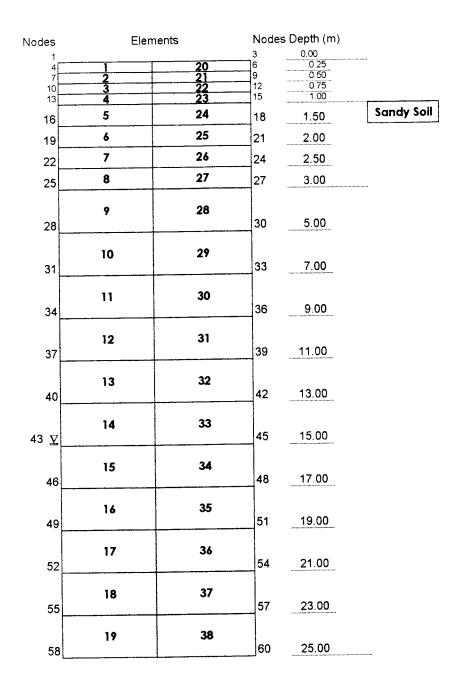


Figure 5-1. Finite Element Method Development Original Conditions

INITIAL CONDITIONS.

As stated earlier, the surface contamination of TNT was measured at 500 to 1,400 μ g/g soil. Localized hot spots were identified at concentrations exceeding 35,000 μ g/g. For the purposes of this study, initial concentrations were averaged over the entire model area.

TNT concentrations in the deeper soils were measured at less than 50 $\mu g/g$ soil. Soil-water concentrations of TNT were approximated using the following relationship:

$$\log C_s = \log K + 1/n \log C_e \tag{12}$$

Where the K \approx 1.08, and 1/n \approx 0.83. A plot of this equation on log-log paper results in a straight line where K is the y intercept and 1/n is the slope of the line. C_s is the concentration adsorbed onto the soil particle and C_e is the amount of contaminant in solution (Environmental Sciences et al. 1991).

TNT is very recalcitrant and has a natural decay rate that Howard et al. (1991) reports as being from 4 weeks to 180 days. This is based on Spanggord's studies of freshwater organisms and does not directly apply to the application at hand. Therefore, a more conservative half-life decay rate of 360 days was assumed for the initial degradation simulation.

TEMPORAL MODEL DEVELOPMENT.

After establishing the spatial elements of the grid system and the initial and boundary conditions of the modeled system, development of the temporal

parameters are necessary. Influencing factor(s) that have the most effect on determining the period of time to simulate in the model are most often related to reported climatological data.

Climatological data required for the model included monthly precipitation, evaporation, and temperatures. This type of climatological data is often available from the state climatologist. Precipitation data received for this study dated from 1947 to present, evaporation data reported was "hit and miss" in completeness, and temperatures were complete except for minor instrumental errors resulting in non-recordings.

Arid regions typically have short duration storm events. Even though the average annual precipitation is less than 10 inches, the combination of storm duration, intensity, and soil permeability contribute to storm events producing localized runoff conditions. The amount of runoff is not accounted for by the climatological recording devices. Therefore, an estimate of the amount of infiltration being adsorbed into the soil was used. An incremental approach was implemented to determine the amount of precipitation that infiltrated the washout lagoon soils. For each half inch increment of rain received a 10% loss was incurred after the first half inch of rain. The initial quantity (0.5") of water infiltrated at 100%, the second increment infiltrated only 90%, and so on. In general, an overall reduction of 9 to 12% could be applied to all the monthly precipitation measurements. Climatic Data for the last eleven years was utilized and the adjusted and raw climatic data are attached in Appendix C.

CONTAMINANT PARAMETERS.

The model will use TNT as the primary contaminant. Knowing the intrinsic properties and behavioral characteristics of TNT with the surrounding environmental conditions are necessary to adequately model the degradation effects in the contamination zone.

Specifically, contaminant parameters such as solubility and partitioning coefficients describe how the chemical distributes itself between two mediums. Three partitioning coefficients are important to waste managers and remediation professionals. These are the octanol-water partition coefficient (K_{ow}), soil-water partitioning coefficient (K_{p}), and the vapor-liquid partition coefficient. BIOROOT utilizes the octanol-water partition coefficient as its main parameter affecting the contaminant interactions with the surrounding environment (LaGrega et al. 1994). The octanol-water partition coefficient is a dimensionless constant defined by:

$$K_{ow} = \frac{C_o}{C_{w}}$$
 (13)

Where the ratio of the concentration of the chemical in octanol, C_o is compared to the chemical's concentration in water, C_w. This octanol-water relationship has been further expanded upon to make estimates concerning other parametric factors such as the root concentration factor and the plant's transpiration stream concentration factor. Once these two parameters are

known, the concentration of the contaminant in the structure of the plant can be determined from Equations 3-2 and 3-5 as described earlier.

Another important factor impacting the degradation of explosive compounds is their relatively long half life in natural environments. Simply stated, half lives are the amount of time required for the compound to degrade to half of the compound's original concentration. Most of the half-lives for explosive compounds are not known or are estimates derived from other environmental conditions. For instance, the half-lives for TNT are based on freshwater conditions. Therefore, applying these parameters to different environmental conditions is, at the least, slightly suspect.

ADSORPTION ISOTHERM COEFFICIENTS.

The geotechnical profile indicates that the soil is a highly permeable sand with very low organic content. The organic content and adsorption potential is documented through Environmental Science's (1991) adsorption studies of the UMDA soil in which the Fruendlich adsorption isotherm values indicate coefficients of ~1.08 and organic contents of ~0.07% were found. Adsorption coefficients and organic contents in this range do not present a very adsorptive environment for the contaminant to become attached. Therefore, highly permeable sand with very low organic content contributes to a highly mobile advective transport of the contaminant. Contaminant transport is only hindered

upon reaching the saturated zone or when non-flowing conditions exist in the soil-water pore volume.

VEGETATION.

The presence and density of arid vegetation is not well documented in the RI/FS reports. The only vegetation reference is to arid grasses and shrubs that exist in the general area. For the purposes of this study, it will be assumed that arid vegetation contributes to the organic factor (adsorption sites) of the upper soil, thus conservatively retaining more contaminant than ordinarily incorporated into the model.

Root Parameters.

There are three main components of the plant that are involved with the uptake and transformation of contaminants from the soil. The most important aspect of the plant is the root system. Root systems vary a great deal between plant species. Plants with a higher density of root mass per unit volume of soil provide a greater amount of adsorption sites for the contaminant within the soil matrix.

SIMULATION SCENARIOS.

In order to demonstrate the various remedial effects of contaminant decay, amendment addition, and vegetative uptake on the contaminant, four scenarios were simulated using the BIOROOT model. Temporal durations were based on monthly climatic data (Taylor, 1995). Monthly inputs for a total duration of 11

years were used in the model, providing adequate temporal and climatic variability to demonstrate the likely transport of the contaminant through the defined spatial system.

Scenario 1: No Degradation.

In the first scenario initial surface contamination is equal to 1,400 μ g/g in the first 0.5 meters (2 feet) of the soil. No initial contamination is present beneath 0.5 m. The degradation rate of the contaminant is zero so that no effective degradation occurs. The only factors affecting the fate and transport of the TNT are the advective-dispersive transport resulting from the infiltration of rain water. This scenario demonstrates whether the contamination in the surface soils is a likely contaminant source to the underlying soil and ground water and is the baseline scenario to be compared to the other simulations.

Scenario 2: Degradation with a Half Life of 1 Year.

The second scenario analyzes the effect of changing the degradation of the contaminant from no degradation to a half-life of 1 year. The effects of this change illustrates the remedial impacts associated with properly applied degradation rates of the model.

Scenario 3: Addition of Soil Amendments.

The effects of amending the soil with 10% organic material as demonstrated by Banwart et al. (1991) shall provide increased adsorption sites

and the minimum soil matrix that will support vegetative growth. Organic soil amendments are added to the top 3 feet of soil which has a slight dilution effect on the soil-contaminant concentration. However, the Initial concentration will not be reduced according to the linear dilution relationships in order to directly compare the results between the various scenarios. The 10% organic soil amendments will increase the adsorption characteristics of the soil by providing additional adsorption sites for the contaminants to attach. This amendment increase has been artificially represented as a soil having characteristics of a "sandy loam" soil for the model. Figure 5-2 illustrates the changes in the spatial development from the addition of soil amendments (sandy loam) to the area of interest which will also influence the test scenarios 3 and 4. Maximum amendment augmentation does not exceed 10% as no additional benefit to the remediation effectiveness in establishing plant growth was determined (Banwart et al. 1991) and costs associated with introducing external ingredients to the soil are minimized.

Scenario 4: Establishing Remedial Vegetation.

As stated above, the amendments to the soil provide a soil matrix that is more conducive to establishing vegetative populations, such as alfalfa (Banwart et al. 1991). The addition of vegetative remediation to scenario 3 demonstrates the overall effects of incorporating vegetative degradation in the upper soil contamination zone and evaluating whether vegetation is capable of minimizing

Nodes	Elem	Elements		Depth (m) 0.00	
1 4	1	20	3 6	0.25	
7	2	21 22	9	0.50 0.75	
10 13	3 4	23	15	1.00	Sandy Loam
16	5	24	18	1.50	Sandy Soil
19	6	25	21	2.00	
22	7	26	24	2.50	
25	8	27	27	3.00	desilien blee
28	9	28	30	5.00	
31	10	29	33	7.00	
34	11	30	36	9.00	
37	12	31	39	11.00	
40	13	32	42	13.00	
43 ∑	14	33	45	15.00	
46	15	34	48	17.00	
49	16	35	51	19.00	
52	17	36	54	21.00	
55	18	37	57	23.00	
58	19	38	60	25.00	

Figure 5-2. Finite Element Method Development Soil Amendments

or reversing the downward leaching of the contaminant into the deeper soils and ground water supplies.

Alfalfa will be utilized as the plant species of choice as it has well documented remedial properties, known parameters, and is easily managed by conventional agricultural equipment (Tracy et al. 1992, 1994, and Banwart et al. 1991). Figure 5-3 illustrates the changes in the spatial development from the addition of alfalfa to the test zone during the last test scenario 4.

Alfalfa's root density was approximated as being 0.080 in the first 0.25 meter, 0.071 from 0.25 m to 0.5 m, and 0.055 from 0.5 m to 0.75 m. Below 0.75 meters, the roots are not typically present in the soil. Therefore, the root density is set to zero for all depths below 0.75 m. This does not infer that the roots do not have an effect on the soil and soil-water below the 0.75 m depth.

Nodes 1 4 7 10	Eler 2 3	20 21 22	Nodes 3 6 9	Depth (m) 0.00 0.25 0.50 0.75
13			15	1.00
16	5	24	18	1.50
19_	6	25	21	2.00
22	7	26	24	2.50
25_	8	27	27	3.00

Figure 5-3. Finite Element Model Development, Establishment of Alfalfa Foot Zone.

CHAPTER 6.

DISCUSSION OF RESULTS

In order to analyze the output from the BIOROOT model, the concentration history and contour plot files for each simulation were imported into a spreadsheet and manipulated to produce the graphical results presented in this chapter. Simultaneous comparisons of the four scenarios were then possible.

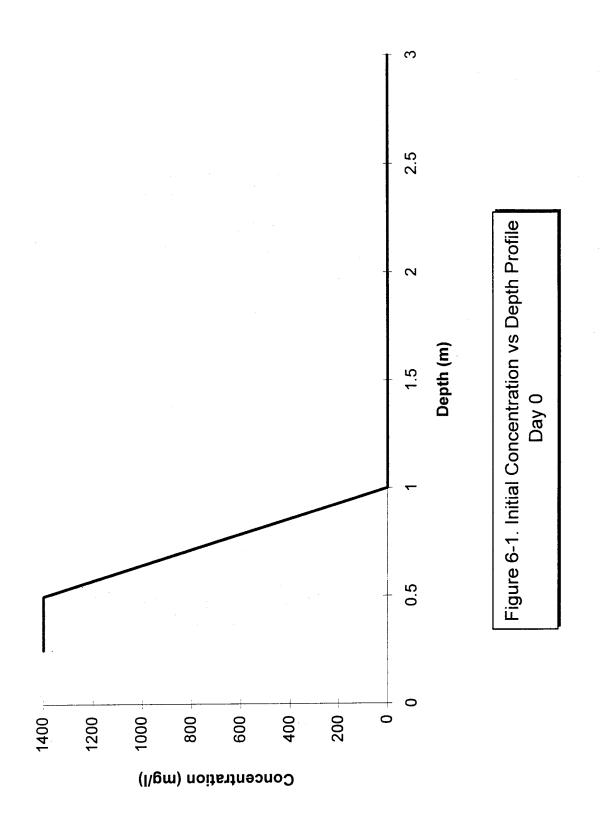
For all the scenarios, the output was formatted to monitor the results of the pressure heads and contaminant concentrations at depths of 0.25, 0.5, 0.75, 1.00, 1.50, 2.00, 2.50, and 3.00 meters. Figures 6-1 through 6-10 track the variations of the TNT concentration as a function of both time and increasing depth. The model can also track the mass flux and the cumulative mass of the contaminant passing an arbitrary boundary condition. This boundary was set at a depth of 3.0 meters. Water fluxes through the zone of interest are from storm event infiltration, evaporation, and plant root transpiration. Figures 6-11 and 6-12 monitor the mass flux and the accumulating mass of system.

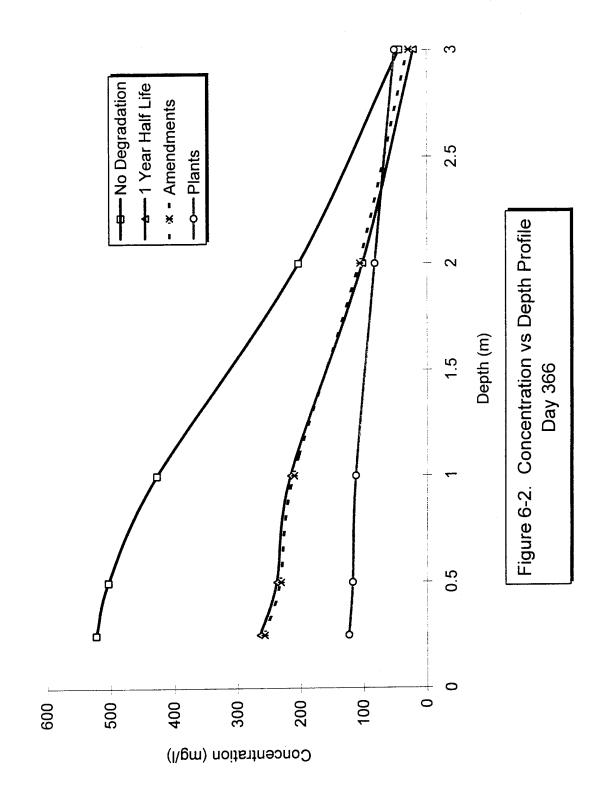
Significant contaminant concentrations were not observed at depths greater than 3.0 meters, therefore, summary figures do not indicate depths greater than 3.0 meters. The response of the various scenarios are compiled on the concentration profile figures at specific time intervals and depths. These profiles provide a "snapshot" summary of the contaminant's behavior as it moved through the area of interest.

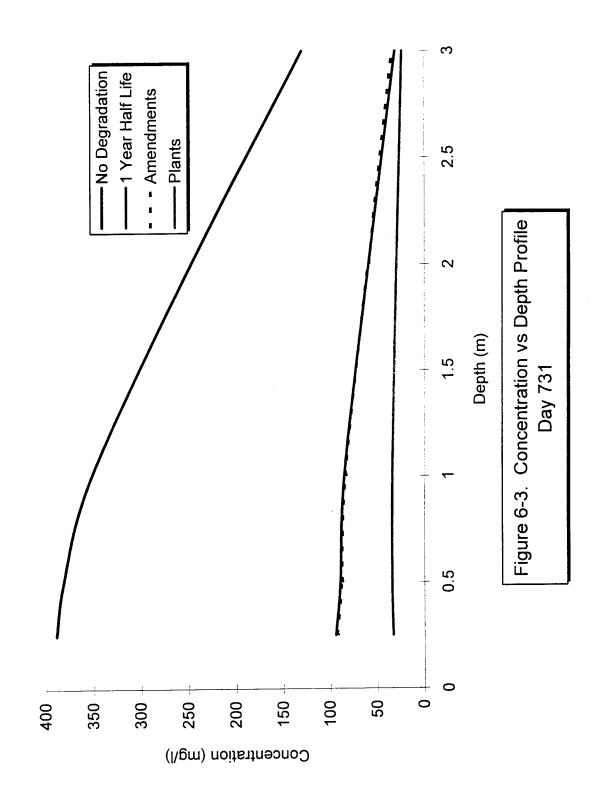
TNT CONCENTRATION VERSUS DEPTH PROFILES.

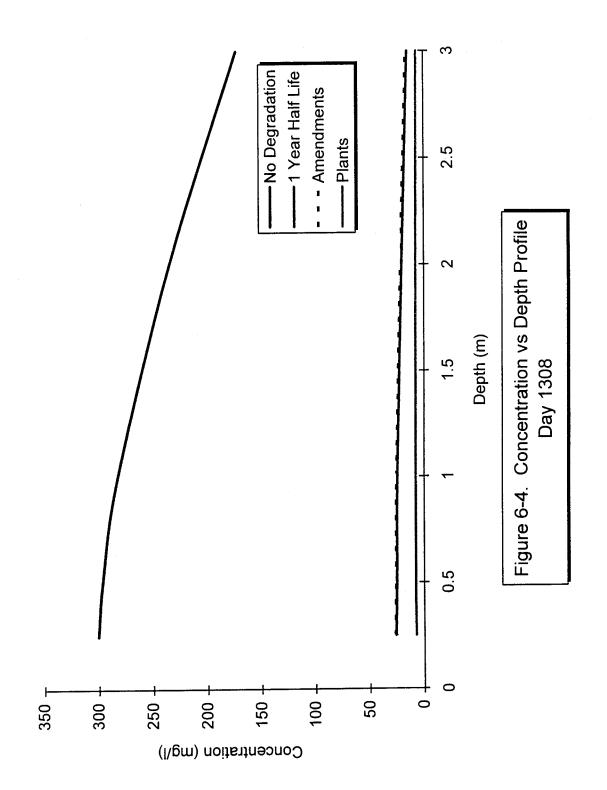
Examining the "No Degradation" responses in Figures 6-1 through 6-5, a noticeably higher concentration profile exists that is greater than the other scenario profiles. During the first year the advective-dispersive processes dispersed the TNT resulting in a decrease of 63% of the material leaching from the 0.25 m depth. The initial 1400 mg/l TNT contamination in the upper soil regions decreased to 600 mg/l (0.25 m depth) and dispersed to a concentration of approximately 50 mg/l at the 3 meter depth. Subsequent time steps show the concentration curves flattening and dispersing the contaminant by approximately 24% (0.25m depth). Although not plotted, the concentration after 11 years was estimated to range from 199 mg/l at 0.25 meters to 166 mg/l at 3.0 meters. The last three years of the simulation resulted in dispersing only 10% of the remaining TNT from the 0.25 meter depth.

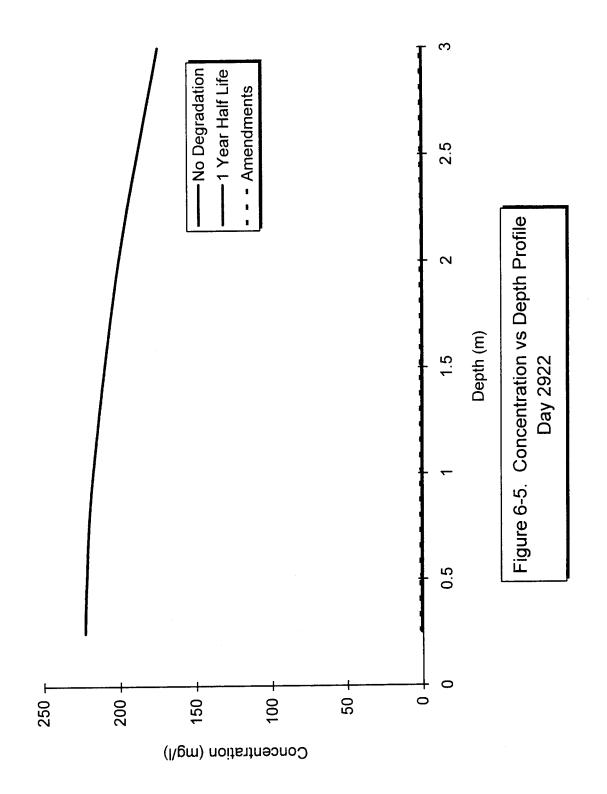
The other test scenarios, all of which involve a decay term, demonstrate that degradation has a significant influence on reducing the overall contamination level in the soil profile. When comparing the 1 year half life to No Degradation scenario, the only difference between the two scenarios is that the 1 year half life has implemented a decay rate at which one half of the contaminant will decay in one year. The difference in concentration between the two curves represent the amount of TNT that has decomposed or broken down









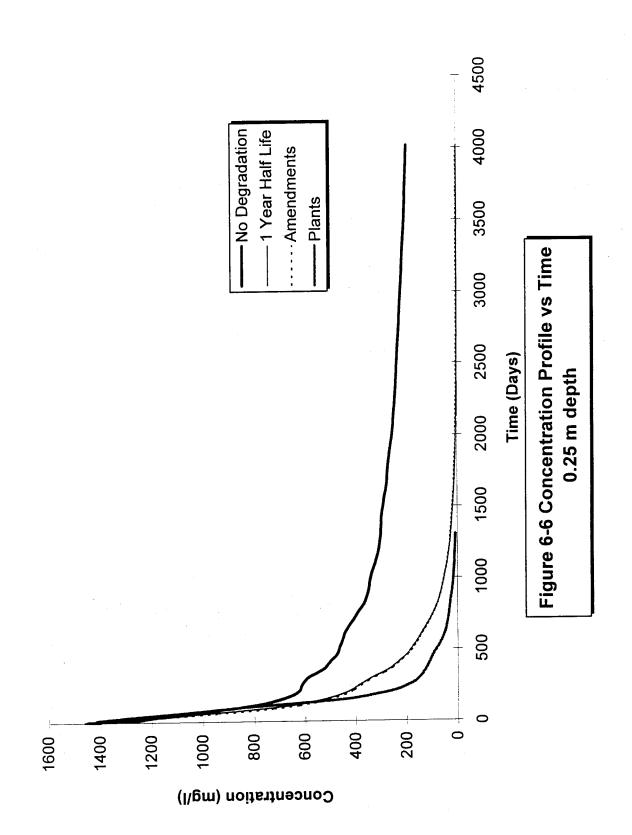


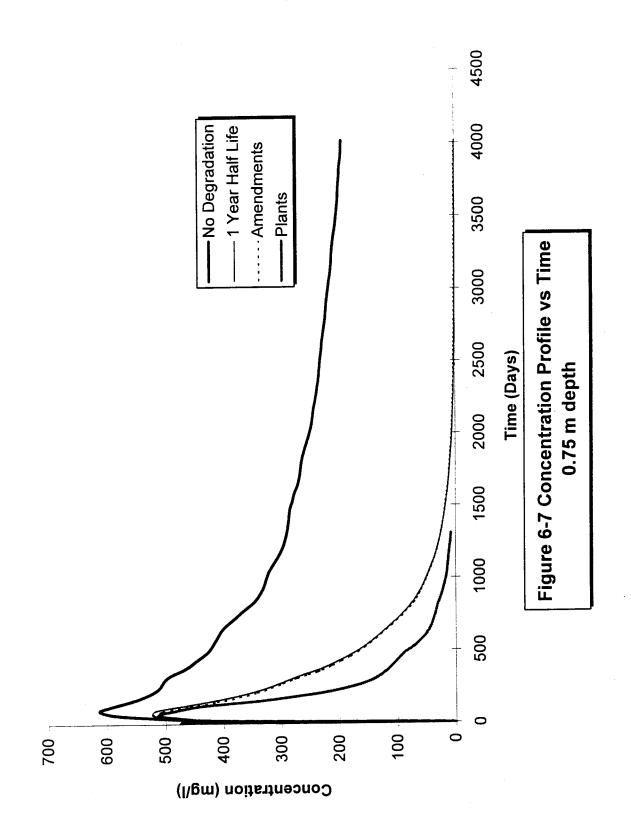
through the nitro reduction or methyl oxidation processes described in the literature review in chapter 2.

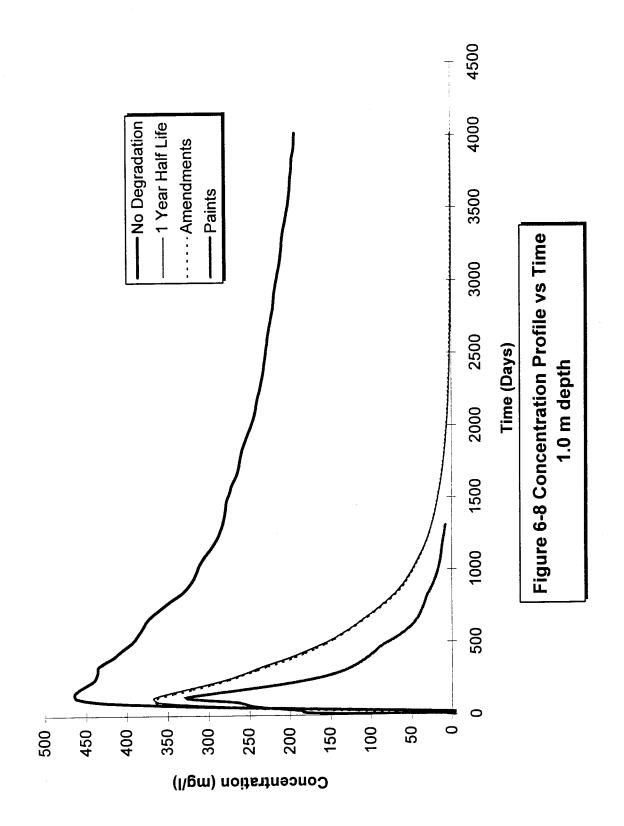
In all the figures presented in this chapter, the impact of amending the soil with 10% organic material offers minimal additional benefit as a stand alone remediation process when compared to the natural degradation of the contaminant. At no time did the amendments contribute significant degradation of the contaminant. Early in the simulations the amendments did decrease TNT concentration leaching to deeper soils. Thus, the amendments were able to retain more of the contaminant in the upper regions of the soil profile thereby making them available for capture by the plant system or natural degradation according to the contaminants half-life value. Amendments are a vital and mandatory step in preparing the site for vegetative remediation processes. This simulation verified the benefits of vegetative remediation were indeed from the alfalfa's uptake of the contaminant and not significantly from the additional adsorption sites provided from the amendments.

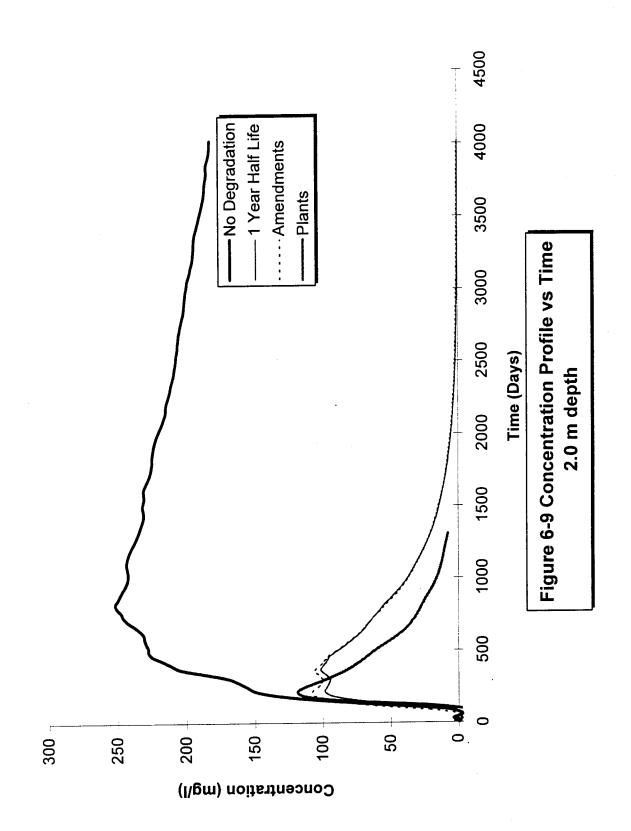
TNT CONCENTRATION VERSUS TIME PROFILES.

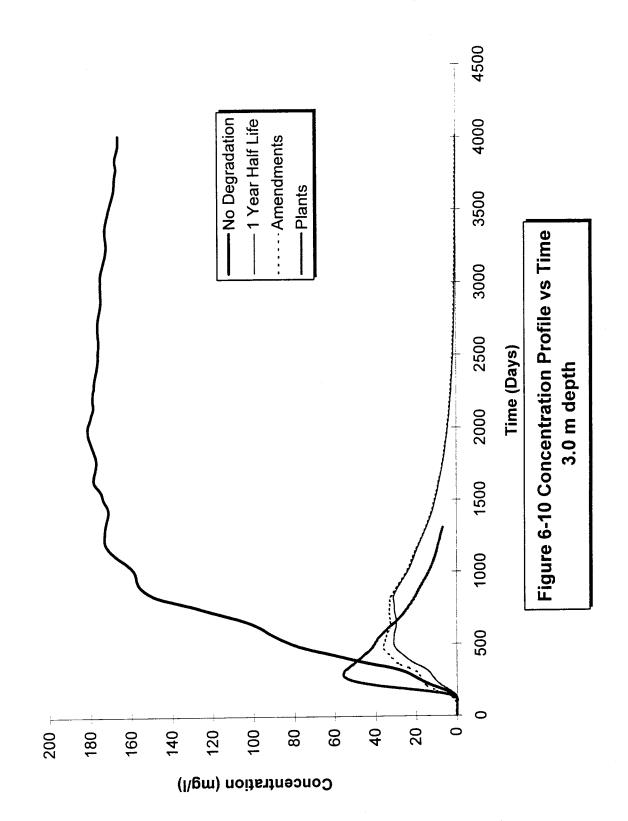
These same relationships can be shown in the Concentration vs. Time profiles. Figures 6-6 through 6-10 also illustrate the advective dispersive relationships with respect to time and depth. Here the depth is held constant so that observations can be made with respect to the time variable. Comparing the responses between initial depths, 0.25 and 0.75 meters, the first observations











concerning the downward movement of the TNT can be made. As TNT reached the 0.75 m depth, the observed concentrations reached a peak of about 620 mg/l and then immediately began to taper off. The initial sharp rise is the result of the initial wave of contaminant moving through the soil from time period 0. This same wave is also seen in all the remaining profiles, however the concentration intensity is reduced. This reduction is caused by 2 major factors: advection - dispersion transport spreading the plume downward and the adsorption interactions occurring with the clean soil. If the TNT contamination had responded as a plug flow contaminant, a very discernible wall effect would have been observed. Additionally, after the slug of TNT had passed, the concentration remaining in the soil could be attributed to the adsorbed phase.

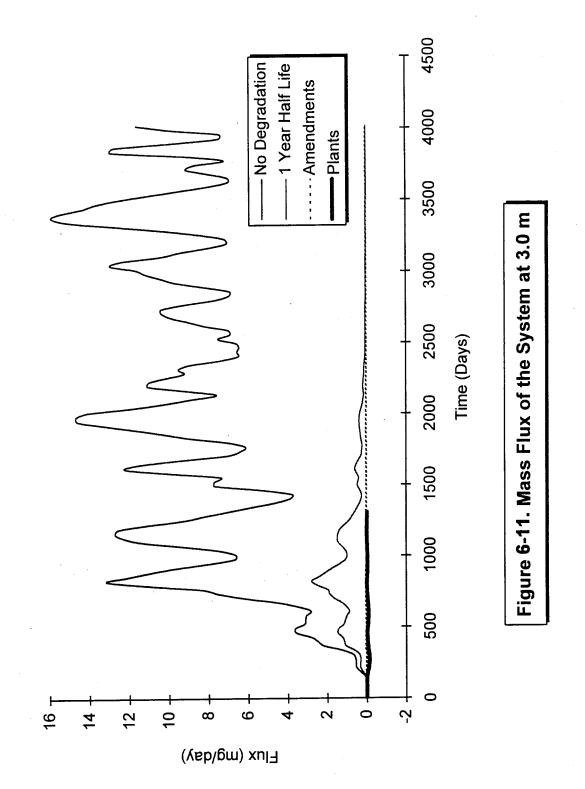
The introduction of alfalfa plants into the study further decreases the concentration intensity of the plume. This can be attributed to not only the roots ability to capture TNT from the soil water phase but also the roots provide additional adsorption sites onto the root's structure.

An anomaly occurred in Figure 6-10 where the plant's curve is initially steeper than the No Degradation simulation. This indicates that the plants are causing the TNT to transport faster than the No Degradation response. There appears to be no viable reason for this to occur. Plant - contaminant interactions normally slow rather than accelerate the transport of the contaminant.

MASS FLUX OF TNT.

The BIOROOT model is capable of tracking the mass flux of the contaminant as it passes between two elements. In this study, mass flux was calculated at the lower boundary at a depth of 3.0 meters. The mass flux response is graphed with respect to time and is illustrated in Figure 6-11. All four scenarios exhibit a lag time of approximately 20 days which represents the amount of time required for the TNT to reach the 3.0 meter depth via advection and dispersion. The mass flux for the four scenarios are shown in Figure 6-10.

After the initial lag phase passed, the mass flux varies greatly between the different scenarios. The No Degradation response is highly erratic in its pattern. This can be attributed to a direct relationship with storm events and the amount of infiltration that is carrying the contaminant deeper into the underlying soil. The first major peak (4 mg/l, ~500 days) is the initial "breakthrough" of the TNT as adsorption sites in the upper soil regions are being exhausted. Breakthrough is a very common response with adsorption processes in traditional industrial wastewater treatment. Subsequent TNT mass fluxes continue to contribute to loading the adsorption sites within the soil matrix until complete exhaustion occurs. Adsorptive exhaustion is when the soil can no longer attract a meaningful concentration of contaminant solute from the soil-water phase onto the solid phase of the soil. This adsorption process can be described best by Figure 6-12 (Benefield et al. 1982) of an idealized carbon adsorption column



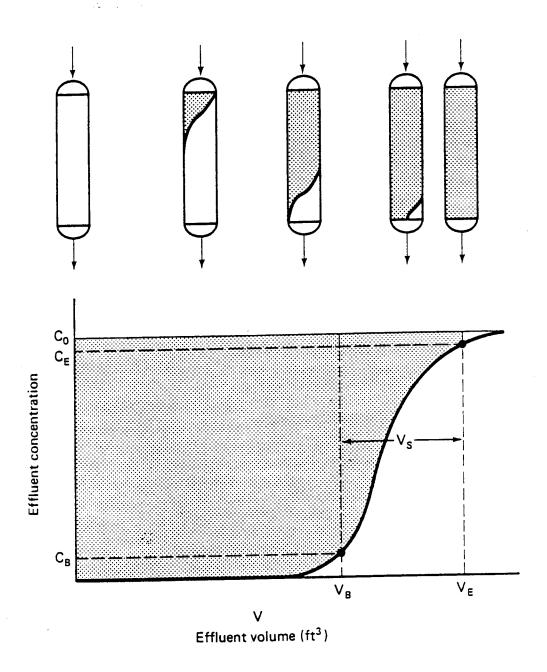


Figure 6-12. Idealized Breakthrough Curve for Carbon Adsorption (Benefield et al. 1982)

undergoing normal loading of a compound. Benefield's column illustration simplifies the adsorption process occurring in the model of the UMDA site. Initially, the deeper soils are uncontaminated and will behave as the first column depicts. As TNT continues to leach into the soil, the TNT will adsorb to organic matter within the soil matrix. The third column illustrates breakthrough of the lower region of the column in the same manner that Figure 6-10 profile indicated. The fifth column graphically shows the column after the media has been completely exhausted and becomes unreactive in adsorbing additional contaminant.

After breakthrough and exhaustion have occurred, the compound will continue to pass through the media as a function of the annual precipitation cycle with little interaction or degradation. The upward slopes (toward the peaks) represent when storm events recharge the soil water and increase the soil water pressure head of the upper soil zones thus moving water and TNT downward. The downward slopes represent the drought cycle when storm events are not contributing significant quantities of water, thus decreasing the upper soil water pressure head on the system. Therefore, the "No Degradation" scenario exhibits classic advective - dispersive behavior as a conservative contaminant after breakthrough has occurred.

The other scenarios exhibit similar responses except for the fact that their respective degradation factors are eliminating TNT from the total mass of the system. The mass flux in the vegetation scenario is negative. This indicates that

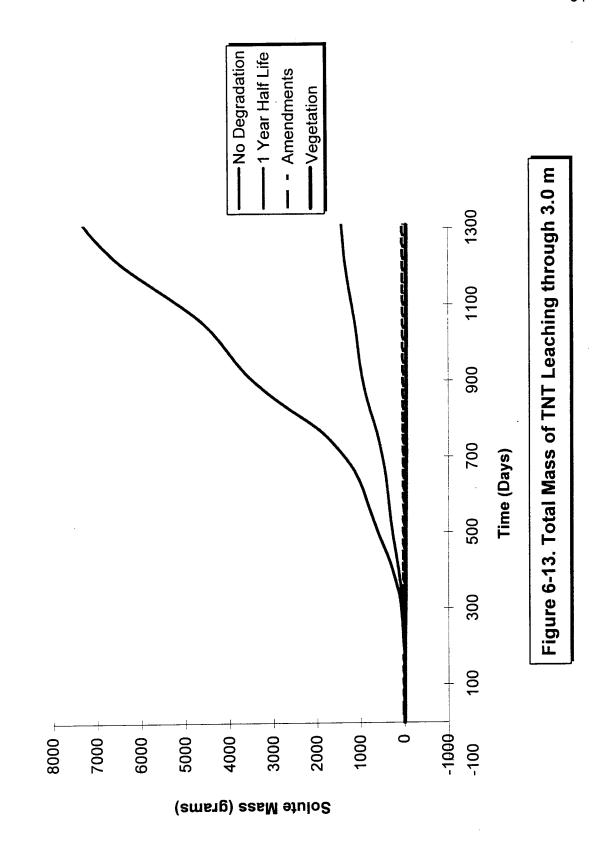
the root zone is capable of extracting TNT from below the 3.0 meter depth.

Although the roots are physically located in the top 0.75 meter of soil. They transport water from soil depths below 0.75 meters. Thus, the roots are behaving as a contaminant sink, drawing the contaminant toward the roots and internalizing the TNT.

TOTAL TNT MASS LEACHING FROM SOIL.

The cumulative mass of TNT passing through the 3.0 m depth is also monitored by the BIOROOT model. By monitoring the total mass of TNT that has passed through a specific depth profile, a true picture of the fate and transport of the contaminant can be understood. Figure 6-13 illustrates the cumulative mass leaching into the deeper soil profiles and possibly the ground water. The "No Degradation" scenario has contributed over 7000 grams of TNT per square (surface) meter to the soils deeper than 3.0 meters. The 1 year half life simulation contributed almost 1000 g, the amendments only 21 g, and the plants were capable of reversing the contaminant migration by removing 49 g from the deeper soils.

The effects of incorporating vegetative remediation technologies is well illustrated in Figure 6-11. In this study the root system was located in the top 0.75 meter but was able to influence and draw up TNT from depths greater than 3.0 meters. This implies that the roots have a capability of influencing contaminant migration toward the root zone up to 3x the actual distance from the



root zone. Vegetation is capable of removing contaminants from distances greater than the physical location of the root system and contain the TNT contaminant "in place" by not allowing further migration and pollution of the underlying soils and ground water sources.

CHAPTER 7.

CONCLUSIONS

The BIOROOT model simulates the fate and transport of contaminants through variably saturated soil conditions exceptionally well. This model behaved according to known field, laboratory, and textbook adsorption concepts. The responsiveness of the No Degradation mass flux scenario indicate that the model responded well to the minor infiltration fluxes associated with the arid climate of the Umatilla Depot Activity and the surrounding Hermiston, Oregon area.

The surface contamination of the explosive washout lagoons at the Umatilla Depot Activity near Hermiston, Oregon may not require expensive exsitu remediation and restoration processes. The continued migration of the explosive contaminants into the ground water may not only be halted but may also be extracted from the soil matrix and remediated by plants. The use of vegetative remediation in this study indicate that the root system's area of influence may be capable of removing contaminants beyond their physical reach. Additional research applying both vegetative remediation and field application in situ modeling, as a daily monitoring tool, in pilot scale and then field demonstration experiments may be warranted based on this research.

The majority of the recent research has been toward identifying microbial populations, such as the white rot fungus and various psuedomonas organisms, capable of in situ remediation of explosive compounds. Little research has focused on vegetation processes other than top soil erosion control. The ability of vegetation to flourish in contaminated environments and metabolize the contaminant may provide more remedial capability and capacity than thought before. Other plant species, such as the wild tomato or fescue and rye grasses may be more tolerant of explosives compounds in this study, which may not require expensive soil amendments or other augmentative precursors. However, the cost of amending the soil with 10% organic material is still less costly than the operating costs associated with pump and treat or other ex situ remediation processes.

The BIOROOT model requires that a complete and thorough understanding of the targeted remediation site be known. The input parameters to this model require exceptional skill in determining valid parameter inputs versus field measured values that are commonly accepted but may not be valid in the circumstances simulated. For instance the range of the hydraulic conductivity for the UMDA site are reported as being large (277 ft/day) to very large (3270 feet/day, ESE 1991). The problem stems from the application of the traditional saturated soil values versus the relative values commonly associated with non-isotropic, non-homogeneous variably saturated conditions. Proper

model calibration is necessary to account for site specific heterogeneity when applying the model to an actual site during hypothetical remediation operations.

BIOROOT was able to predict and illustrate the relative efficiencies associated with alternative remediation processes. The incorporation of vegetative remediation techniques are favorable for TNT contamination and should be sought out and exploited. Results from this research could be applied to determine the cumulative remedial effects of these same processes and provide an updated estimation of the time necessary to remediate the site to an acceptable level.

The BIOROOT model is limited to simulating only one degradation process at a time. This might be overcome through the use of superposition techniques to establish a cumulative degradation factor that can be input into the model. Continued model development should incorporate simultaneous multiple degradation processes. The additional capability of expanding the model to address additional contaminants such as the generation and degradation of intermediate daughter products is warranted. A more complex representation of biological degradation would have been incorporated into this study had the model been able to incorporate multiple degradation reactions This type of modeling would also require biological kinetic data which is not available at this point in time.

RECOMMENDATIONS FOR FUTURE RESEARCH

Additional research could be conducted to determine the modeling efficiencies of BIOROOT on remediating TNT contamination from saturated soils. This would involve establishing an in situ anaerobic biological system in the saturation region. The concentration of the contaminant in the soil-water must be below the threshold level of 200 ppm for biological activity to be initiated (Funk et al. 1993). TNT concentrations of 50 mg/g were reported at depths of 10 to 50 feet (water table). Soil water concentrations in the saturated region measured 50 mg/l. The biological species may be able to remediate munitions contaminating the variably saturated region immediately above the water table (Funk et al. 1993).

A sensitivity analysis should also be completed on the model to determine which parameters are more consequential. This study alone identified that the variation of the half life degradation factor had a significant impact on the overall remediation of the washout lagoons. The model's ability to monitor the mass flux of the system under arid climates indicates the responsiveness and sensitivity of the governing adsorption - dispersion equation. Other parametric variables may or may not have similar significant effects on the model. Those parameters that have pronounced effects on the model must be focused on in order to ensure accuracy and validity. Sensitivity analysis also provides a prioritized method for obtaining and utilizing parametric information. Environmental parameters of

major significance should be obtained from either laboratory, pilot, or field scale experiments or surveys. Priorities can be directed at those parameters and information that will yield the most results for the capital resources obligated. Parameters of minor significance may be estimated if necessary. The acquisition of non-significant parameters can be further prioritized without adversely affecting the validity of the results. All too often financial resources are limited and require responsible decisions to acquire not only the most information possible, but more importantly, the right information.

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APPENDICES

APPENDIX A.

DEFINITIONS OF MODEL PARAMETERS

PARAMETER DEFINITIONS

An alphabetical listing of the parameters and their definitions is listed below.

```
soil porosity
η
θ
       soil-water content
       storativity indicator. \beta = 1 if \psi_s \ge 0, \beta = 0 if \psi_s < 0.
ß
       bulk density of the soil
\rho_b
       root water pressure head
\Psi_{r}
       soil water pressure head
Ψs
       soil characteristic parameters
Α
       soil characteristic parameters
С
С
       solute concentration
       contaminant concentration adsorped onto the root structure
C_r
       contaminant concentration in the plant's transpiration stream
C_{ts}
       Dispersion coefficient
D
       first order decay rate
k
       adsorption coefficient
K<sub>1</sub>
       hydraulic conductivity of the root
K,
       hydraulic conductivity of the soil
Ks
        soil-water extraction rate by the plant's root system
q
       root concentration factor
R_{cf}
       contaminant sink due to plant uptake
S
        effective saturation of the soil. = \theta/n
S.
        specific storage of the soil (storativity)
S<sub>s</sub>
Sv
        specific yield of the soil
       time
t
        plant's transpiration stream concentration factor
Tscf
        Darcy soil-water flux
        root water content
WC<sub>r</sub>
        horizontal spatial dimension
Χ
```

vertical spatial dimension

Z

APPENDIX B.

BIOROOT SIMULATIONS; HISTORY FILES

No Degradation

30			-	0.25		0.5	-	0.75		F	-	1.5		2		2.5	-	က
12	Solute Mass Flux	ass Flux	Node	5	Node	80	Node	11	Node	4	Node	17	Node	20	Node	23	Node	56
-	(ma/dav)	(arams)	(meters)	(Mg/L)	(meters)	(mg/l)	(meters)	mdd										
ı.	0	0	-14.75	g	-14.5	1400	-14.25	0	-14	0	-13.5	0	.13	0	-12.5	0	-12	0
2	0	0	-14.5382	1416.1	-14.3528	1321.6	-14.1476	81.4	-13.9287	-13.3	-13.4654	3.5	-12.9831	6.0-	-12.4918	0.2	-11.9963	0
, 5	0	-0 0002	-14 3945	+	-14.2258	1195.9	-14.0403	221.7	-13.8409	-26	-13.4099	6.4	-12.9498	-1.6	-12.4727	0.4	-11.9859	0
7 4	0	0.0004	-14.285	1394.2	-14.1222	1103.5	-13.9458	329.4	-13.757	-18	-13.348	3.6	-12.9072	-0.8	-12.4448	0.2	-11.9685	0
Š	0 0001	0.0001	-14.194	1361.8	-14.0343	1044.3	-13.8628	399.1	-13.6804	9.9	-13.2864	6-	-12.8607	-	-12.4114	-0.3	-11.9456	0
2,52	0000	0.0016	L	1328.5	-13.957	1005.8	-13.7887	443.5	-13.6105	39.5	-13.2271	-10.3	-12.8131	2.6	-12.375	9.0-	-11.9186	0.1
1 6	0 0005		Ι.	1291	-13.8751	974.7	-13.7092	478	-13.5344	81.7	-13.1601	-17.3	-12.7567	3.7	-12.3293	-0.8	-11.8829	0.1
9	6000 0-	Ľ	┸	1083.5	-12.8571	872.7	-12.7948	284	-12.7124	294.8	-12.495	6.4	-12.219	-2.7	-11.8958	9.0	-11.5351	-0.1
8 6	0 0011	0.0121	1	885	-11.8538	778.4	-11.8419	613.8	-11.8119	427.4	-11.701	118.9	-11.5286	7.8	-11.3022	-0.2	-11.0293	0
12	0.0046		-11 5404	6.797	-11.4973	669	-11.4473	592.9	-11.3897	462	-11.2495	207.2	-11.0737	52.9	-10.8618	5.6	-10.6147	0.1
152	0.0015	_		694.8	-11,2535	643.7	-11,1836	563.9	-11.1085	464.8	-10.9409	255.1	-10.7488	98.7	-10,5308	24	-10.2865	1.8
182	0.3187	Ť,	+	646.6	-11 2172	605.3	-11,1173	540.7	-11,0153	459.1	-10.803	280	-10.5773	131.3	-10.3356	44.5	-10.0764	6.5
213	1	1	+-	622.5	-11.9759	582.5	-11.7629	522.9	-11.5605	449.6	-11.1806	288.4	-10.8234	149.1	-10.4793	59.1	-10.1411	12.5
244			┸	614.9	-12.3581	571.9	-12.1295	511.6	-11.907	440.9	-11.4784	288.1	-11.0679	155.6	-10.671	66.3	-10.2836	17.2
27.4	0.5744	_	4_	909	-12.1247	563.7	-11,9539	506	-11.7789	437.6	-11.4193	290.5	-11.0515	161.8	-10.6786	72.2	-10.3025	21.1
305	┸	┸		586.3	-12.0988	552.4	-11.9241	500.2	-11.748	436.1	-11.3916	295.6	-11.0296	169.9	-10.6626	79.6	-10.2908	25.5
33.5		Ľ	_	554.2	-10.4817	530	-10.5079	489.6	-10.5077	435.6	-10.4399	308	-10.2992	185.9	-10.1019	93	-9.8606	32.6
386	L		+	523 6	,	504.3	-10.7037	472.1	-10.5926	428.1	-10.3713	317.9	-10.1428	203.8	9006.6-	110.1	-9.6414	43.5
30,7	_		-	509.5	1,	489.5	-11.1117	458.4	-10.9387	417.8	-10.6062	317.3	-10.2854	211.2	-9.9698	120.2	-9.6544	53
425	Ľ		Ι.	495.2	-10.5629	477.7	-10.4966	449.2	-10.4173	411.5	-10.2269	317.8	-10,0029	217.3	-9.753	128.5	-9.4824	61.1
458		1	-	477.5	-10.587	462.7	-10.4739	438.1	-10.3593	404.6	-10.1239	319.2	-9.8776	224.9	-9.6188	138.8	-9.3466	70.8
486		•	1	467.8	-11.179	452.7	-10.9814	428.7	-10.7918	397.2	-10.4311	317.1	-10.0874	227.8	-9.7536	144.9	-9.4243	78.5
517		-	┺-	462.6	-11.4673	446.6	-11.2619	422.3	-11.0605	391.3	-10.6685	313.9	-10.2887	228.2	-9.9181	147.9	-9.5539	83.9
547	_		Ľ	455.3	-11.1216	440.7	-10.9816	417.6	-10.8354	387.5	-10.5281	312.7	-10.2061	229.7	-9.8737	151.4	-9.5336	88.5
578	6,	1 _	╄	448.9	-11.669	434.8	-11.4457	412.6	-11.2298	383.6	-10.8155	311.4	-10.4178	230.9		154.7	-9.6503	92.7
609			1	444.2	Ι.	430.1	-11.3576	408.2	-11.177	380	-10.8105	309.6	-10.4397	231.4	4	156.9	-9.6913	96.1
639	_		1_	434.9	-10.818	423.2	-10.7296	403.7	-10.6287	377.2	-10.3952	310.1	-10.1275	234.3		161.5	-9.5189	100.5
670	<u>L</u>			423.5	-10.5662	413.5	-10.4659	396.5	-10.3603	372.8	-10.1325	310.6	-9.8832	238.4		168		106.6
700		1365.274	١	410.9	-9.5465	402.3	-9.5431	387.5	-9.5237	366.7	-9.4419	310.5	-9.3104	243.1		175.5		114.3
731		1597.31	10.0891	389.5		391.5	1	378.1	-9.7236	359.4	-9.4945	308.5	-9.2651	246.3	1	182	-8.7819	122.5
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 | 237.1 -10.4205 235.5 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 231.6 -9.5411 | 00 | 233.9 | -9.8466 233.9

 | 235.2 -9.8466 233.9 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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 | -9.6398 232.1 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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No Degradation

2646	0 1115	********	0 7530	232 6	-9 6232	231.3	-9.4913	229.2	-9.3573	226.2	-9.082	217.6	-8.7956	206.1	-8.4976	192.1	-8.1882	176.1
2647	8 9969 ******	********	-9 3474	231.4	-9.2565	230.2	-9.1585	228.2	-9.0541	225.3	-8.8277	217	-8.5804	205.7	-8.3147	192.1	-8.0326	176.3
2677	9.8677	********	9.278	230.3	-9.1692	229.1	-9.0577	227.2	-8.9435	224.4	-8.7059	216.3	-8.4555	205.4	-8.1921	192	-7.9157	176.4
2708		*******	9.1469	229.1	-9.0413	227.9	-8.9324	226	-8.8204	223.3	-8.5867	215.5	-8.3404	204.8	-8.0818	191.8	-7.811	176.5
27.3A		*******	-93151	228	-9.1778	226.8	-9.0413	224.9	-8.9052	222.3	-8.6326	214.7	-8.3573	204.2	-8.0773	191.4	-7.7912	176.4
2769	9 2272	********	-9.9174	227	-9.7139	225.7	-9.5177	223.8	-9.3278	221.2	-8.963	213.7	-8.6131	203.4	-8.2729	190.7	-7.9385	176.1
2800	7 7068	7 7068 ********	-10.1457	226.2	-9.9478	224.9	-9.7526	222.9	-9.5601	220.2	-9.1825	212.8	-8.8135	202.6	-8.4513	189.9	-8.0943	175.6
2830	6 9539	********	-10,1683	225.5	-9.9887	224.3	-9.8086	222.2	-9.6284	219.6	-9.2679	212.1	-8.9081	201.9	-8.5492	189.3	-8.1911	175.2
2861	6 908B	6 908B *******	-10 0639	224.8	-9.9056	223.6	-9.7448	221.7	-9.5817	219	-9.2499	211.5	-8.912	201.4	-8.5692	189	-8.2224	174.9
2804	8 1813	********	-9 2165	224	9 1579	223	9.0859	221.1	-9.002	218.5	-8.8031	211.1	-8.5702	201.2	-8.3102	189	-8.0285	174.8
2022		********	9.3	223.1	-9.1838	222.1	-9.067	220.4	-8.9487	217.9	-8.7059	210.7	-8.4523	500.9	-8.1866	189	-7.9082	175
2063	10 4125	******	-8 9973	222	-8.9088	221	-8.8148	219.3	-8.7158	216.9	-8.5033	210	-8.2734	200.5	-8.0273	188.8	-7.7662	175
2082	11 1558	*******	-8.8686	221	-8.7749	220	-8.6778	218.4	-8.5772	216.1	-8.3656	209.3	-8.1399	200.1	-7.9004	188.6	-7.6472	175.1
3013	11 6738 ********	*******	-8.7501	219.9	-8.6555	218.9	-8.5579	217.3	-8.4572	215.1	-8.2464	208.5	-8.0231	199.5	-7.7874	188.3	-7.5392	175
3043	12 9535 *******	********	8.0649	218.8	-8.0358	217.9	-7.9964	216.4	-7.9477	214.2	-7.8249	207.8	-7.6722	1.661	-7.4936	188.1	-7.2921	175.1
3074	12.362	12 362 ********	-9.3559	217.6	-9.1391	216.7	-8.9374	215.2	-8.7482	213	-8.3989	506.9	-8.077	198.3	-7.7723	187.5	-7.477	174.8
310	10.4197	********	-9 1561	216.7	-9.02	215.6	-8.8803	214	-8.738	211.9	-8.4487	205.8	-8.1556	197.3	-7.8605	186.6	-7.5639	174.3
31.35	9 4277	*******	-9 6351	215.9	١٩	214.9	-9.2587	213.3	-9.0777	211.1	-8.7268	205	-8.387	196.6	-8.0549	185.9	-7.7277	173.7
3166	7 9603	*******	-10.08	215.2		214.1	-9.6544	212.5	-9.4497	210.3	-9.0539	204.2	-8.6733	195.8	-8.3045	185.1	-7.9445	173.2
3100	7.055R	*******	-10 0406	214.7	-9.8625	213.6	-9.6833	211.9	-9.5033	209.7	-9.1427	203.5	-8.7827	195.1	-8.4242	184.5	-8.0674	172.6
2227	7 1005	********	-9 8347	214.1	-9 6901	213.1	-9.5414	211.5	-9.3892	209.2	-9.0759	203.1	-8.7531	194.7	-8.4231	184,2	-8.0874	172.3
3257	R 4506	******	-0 1704	213.4	-9 0982	212.5	-9,0152	211	-8.9225	208.8	-8.7116	202.7	-8.4722	194.4	-8.2097	184.1	-7.9282	172.2
3000	40 4318	********	-8 7144	2126	1_	211.8	-8.5896	210.4	-8.516	208.3	-8.3477	202.4	-8.1529	194.2	-7.9342	184.2	-7.6939	172.3
3310	12 AR75	*****	-7 9173	2116		210.9	-7.8947	209.5	-7.8675	207.6	-7.7834	201.9	-7.6635	194.1	-7.5112	184.3	-7.33	172.6
20.00	45 4475		7 7755	210.6		209 9	-7 648	208.6	-7.6031	206.8	-7.4991	201.4	-7.3746	193.8	-7.2285	184.3	-7.0607	172.8
3378	15 9085	********	-7 7654	209.4		208.6	-7.6273	207.4	-7.5565	205.6	-7.4092	200.4	-7.2524	193.2	-7.084	184	-6.9025	172.8
340	15 4513	*******	-8 0129	208.2	_	207.5	-7.8068	206.2	-7.7056	204.5	-7.5046	199.4	-7.303	192.3	-7.0981	183.3	-6.8877	172.5
3439	14 3319	*******	-8,2508	207.1	1_	206.4	-8.0092	205.1	-7.8903	203.4	-7.6551	198.4	-7.4216	191.4	-7.1876	182.6	-6.9515	172
2469	13 6918	13 6918 *******	-8.1483	206.2	L.	205.4	-7.9516	204.2	-7.8494	202.5	-7.6385	197.5	-7.4199	190.6	-7.1944	181.9	-6.9621	171.5
3500	12 5532	********	-8.8561	205.3	_	204.5	-8.5057	203.2	-8.3408	201.5	-8.0265	196.6	-7.7276	189.8	-7.439	181.1	-7.1567	171
3531	11 0805	**********	-8.9012	204.4	-8.7549	203.6	-8.6081	202.3	-8.4613	200.6	-8.168	195.7	-7.8761	189	-7.5856	180.3	-7.2961	170.4
3561	9.5366	**********	-9.6916	203.8	-9.4636	202.9	-9.2459	201.6	-9.0371	199.9	-8.6418	195	-8.2699	188.2	-7.9155	179.6	-7.5739	169.7
3592	7.9775	7.9775	-9.7858		-9.5962	202.2	-9.4074	200.9	-9.22	199.1	-8.8499	194.2	-8.4868	187.4	-8.1308	178.8	-7.781	169.1
3622	6.9688	6.9688	-10.216		-9.9933	201.8		200.4	-9.5647	198.6	-9.1547	193.6	-8.7597	186.8	-8.3766	178.2	-8.0031	168.6
3653	7.0214	*********	-9.6093	202.2	-9.4931	201.4	-9.3673	200	-9.2336	198.2	-8.9472	193.2	-8.6421	186.4	-8.324	177.8	-7.9968	168.2
3684	8.1314	********	-9.4411	201.7	-9.3218	201	`]	199.7	-9.0717	197.9	-8.8064	192.9	-8.5272	186.1	-8.2356	177.8	-7.933	168
3712	9.116	*********	-9.1655	201.2	-9.0678	200.5	-8.9644	199.2	-8.8558	197.5	-8.6239	192.6	-8.3744	185.9	-8.1092	177.7	-7.8301	167.9
3743	8.6716	********	-10.0041	200.5	-9.7882	199.7	-9.5827	198.5	-9.3857	196.8	-9.0114	192	-8.6559	185.5	-8.3119	177.3	-7.9744	167.7
3773	7.1753	**********	-10.2037	199.9	-10.0035	199.1	-9.8059	197.8	-9.6109	196.1	-9.2284	191.4	-8.8549	184.9	-8.4887	176.7	-8.128	167.3
3804	9.102	*********	-8.1461	199.4	-8.2061	198.8	Ė	197.7	-8.2444	196	-8.1944	191.2	-8.0763	184.8	-7.9058	176.8	-7.6949	167.3
3834	12,9025	**********	-7.9795	199		198.4	-7.9139	197.4	-7.8748	195.8	-7.7792	191.2	-7.6574	184.9	-7.5078	177.2	-7.3307	167.7
3865	12.7745	*********	-9.0653	197.9	-8.8799	ľ	-8.7067	196.2	-8.5435	194.8	-8.2404	190.5	-7.958	184.4	-7.687	176.8	-7.4202	167.6
3896	9.7915	9.7915	-9.845	197.1	-9.6126	196.3	-9.3905	195.2	-9.1779	193.7	-8.7769	189.5	-8.4021	183.5	-8.0473	175.9	-7.7067	167.1
3926	7.4525	*********	-10.1316		L	195.7	-9.7016	194.5	-9.4927	193	-9.087	188.8	-8.6961	182.8	-8.318	175.1	-7.9505	166.5
3957	7 4065	2 *********	9.4168	196.2		195.5	-9.2052	194.3	-9.0846	192.7	-8.8207	188.4	-8.5343	182.4	-8.2321	174.8	-7.9186	166.1
3987	9.8492	2 ********	-8.3372			Ĺ	-8.3118	194.2	-8.2767	192.6	-8.1671	188.3	-8.0128	182.3	-7.8214	174.9	-7.5996	166.1
4018	11 6235	2 *********	-8.7549			194.6		193.6	-8.4125	192.2	-8.191	188	-7.9662	182.2	-7.7338	175	-7.4909	166.2
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1 Year Half Life

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1 4	Solute M	Solute Mass Flux	Node 5	T	Node 8	Π	Node 11	-	Node 14	_	Node 17	-	Node 20		Node 23	_	Node 26	
(Days)	(mg/day)	(grams)	(meters)	mdd	(meters)	шdd	(meters)	mdd	(meters)	mdd	(meters)	mdd	(meters)	mdd	(meters)	mdd	(meters)	шфф
0	0		-14.75	1400	-14.5	1400	-14.25	0	-14	0	-13.5	0	-13	0	-12.5	0	-12	0
5	0	0	-14.5382	1402.8	-14.3528	1309.3	-14,1476	80.5	-13.9287	-13.2	-13,4654	3.5	-12.9831	6.0-	-12.4918	0.2	-11.9963	0
10	0	-0.0002	-14.3945	1390.7	-14.2258	1173.9	-14.0403	217.2	-13.8409	-25.6	-13.4099	6.3	-12.9498	-1.6	-12.4727	4.0	-11.9859	0
15		L	-14.285	1355.5	-14.1222	1073	-13.9458	319.8	-13.757	-17.6	-13.348	3.5	-12.9072	-0.8	-12.4448	0.2	-11.9685	0
20	0.0001	0.0001	-14.194	1311.7	-14.0343	1005.9	-13.8628	383.9	-13.6804	6.1	-13.2864	-2.8	-12.8607	0.0	-12.4114	-0.2	-11.9456	0
25	L	0.0015	-14.115	1267.7	-13.957	959.7	-13.7887	422.7	-13.6105	37.3	-13.2271	8.6-	-12.8131	2.5	-12.375	9.0-	-11.9186	0.1
31		L	-14.0317	1218.1	-13.8751	919.6	-13.7092	450.5	-13.5344	76.6	-13.1601	-16.3	-12.7567	3.5	-12.3293	-0.8	-11.8829	0.1
9	Ľ	L	-12.8971	969.8	-12.8571	780.3	-12.7948	521.6	-12.7124	262.3	-12.495	4.3	-12.219	-2.4	-11.8958	9.0	-11.5351	Ģ
16		\perp	-11.8471	748.4	-11.8538	658	-11.8419	517.9	-11.8119	359.8	-11.701	98.2	-11.5286	5.4	l	-0.2	-11.0293	0
121		\perp	-11 5404	614.4	-11.4973	558.9	-11,4473	473.5	-11.3897	368.1	-11.2495	163.5	-11.0737	40.5	-10.8618	3.8	-10.6147	0.1
152	\perp	1	-113184	525	-11.2535	486.1	-11.1836	425.2	-11.1085	349.8	-10.9409	190.6	-10.7488	72.5	-10.5308	11	-10.2865	
100		1	-11 3156	462.1	-11 2172	432 2	-11.1173	385.6	-11,0153	326.9	-10.803	198.1	-10.5773	91.8	-10.3356	30.4	-10.0764	4.1
213	L		-12 2018	419.9	-11.9759	392.7	-11.7629	352	-11,5605	302.1	-11.1806	192.7	-10.8234	98.6	-10.4793	38.4	-10.1411	7.7
244		1	-12 5932	391.4	-12,3581	363.8	-12.1295	325.1	-11.907	279.7	-11.4784	181.7	-11.0679	97.2	-10.671	40.8	-10.2836	10.2
274			-12.29	363.5	-12.1247	339.1	-11.9539	304	-11.7789	262.4	-11.4193	173.3	-11.0515	92.6	-10.6786	42.1	-10.3025	11.9
305	L	\perp	-12.2722	333.1	-12.0988	313.6	-11.9241	283.6	-11.748	246.8	-11.3916	166.5	-11.0296	94.9		43.9	-10.2908	13.7
335		↓.	-10.4255	7.792	-10.4817	284.5	ŀ	262.5	-10.5077	233.2	-10.4399	1.491	-10.2992	98.3	-10.1019	48.6	9098.6-	16.6
386		٦	-10 9366	265.4	-10.8176	255.5	1.	238.9	-10.5926	216.4	-10,3713	160	-10.1428	101.9	9006.6-	54.4	-9.6414	21
702	Ľ		-11.477	243.8		234.1	<u>L</u>	219	-10.9387	199.3	-10.6062	150.8	-10.2854	99.7	-9.9698	56.2	-9.6544	24.3
425			-10 6141	224.8	7	216.7	-10.4966	203.6	1	186.3	-10.2269	143.4	-10.0029	97.4	-9.753	57.1	-9.4824	26.7
456	L		-10.6998	204.6		198.1	-10.4739	187.5	-10.3593	172.9	-10.1239	135.9	-9.8776	95.2	-9.6188	58.3	-9.3466	29.3
486	L		-11 3862	189.5		183.3	-10.9814	173.4	-10.7918	160.5	-10.4311	127.7	-10.0874	91.3	-9.7536	57.6	-9.4243	30.8
517			-11.677	176.8	11	170.6	-11.2619	161.2	-11.0605	149.2	-10.6685	119.3	-10.2887	86.3	-9.9181	55.5	-9.5539	31.1
547			Ľ	164.6	-11.1216	159.2	-10.9816	150.7	-10.8354	139.7	-10.5281	112.4	-10.2061	82.1	-9.8737	53.8	-9.5336	31
578	Ĺ	_	4-	153.1		148.2	-11.4457	140.6	-11.2298	130.5	-10.8155	105.6	-10.4178	78	-10.0308	51.8	-9.6503	30.7
609		-	₩	143	'	138.4	-11.3576	131.2	-11.177	122	-10.8105	99.1	-10.4397	73.7	Ľ	49.6	-9.6913	30.1
639		Ľ		132.3		128.7	<u> </u>	122.7	-10.6287	114.5	-10.3952	93.9	-10.1275	70.6	-9.8335	48.3	-9.5189	29.8
670		_	_	121.6	-10.5662	118.7	-10.4659	113.7	-10.3603	106.8	-10.1325	88.7	-9.8832	67.8	-9.6133	47.5	-9.3247	29.8
2007	L		┸	111.5	-9.5465	109.2	-9.5431	105.1	-9.5237	99.3	-9.4419	83.9		65.4	_	46.9	-8.9274	30.3
731			Ľ	102.3	-9.9621	100.3	-9.8409	8.96	-9.7236	91.9	-9.4945	78.7	-9.2651	62.6	-9.029	46	-8.7819	30.7
762	L	-	↓-	94.2	-9.2593	92.3	-9.2225	89.3	-9.1749	85	-9.0515	73.5	-8.8958	59.4	-8.7125	44.6	-8.505	30.7
790	2.4635	5 693.6436	-8.0167	86.6	-8.0897	85.2	-8.1449	82.7	-8.1833	79.2	-8.2136	4.69	-8.1883	57.1	-8.1144	43.9	-7.9983	31
821	L	7 780.2489	L	79.2	-8.4924	78	-8.4189	75.9	-8.3489	72.9	-8.2134	64.7	-8.0761	54.2	-7.9297	42.6	-7.7693	31.2
851	\perp	_	-9.3809	73.5	-9.2129	72.2	-9.0546	70.2	-8.9046	67.5	-8.6246	60.2	-8.3638	8.03	-8.1145	40.6	-7.8705	30.5
882		+	L	68.2	-8.9461	67.1	-8.8513	65.2	-8.7519	62.7	-8.5418	99		7.74	-8.0899	38.4	-7.8518	29.4
912		+-	T,	63.7	-9.8417	62.6	-9.6312	60.8	-9.432	58.5	-9.061	52.4	-8.7171	44.8	-8.392	36.4	-8.0791	28.1
843	L	٠	╨	59.6	-9.9798	58.5	-9.8001	56.8	-9.6218	54.6	-9.2704	49	-8.9264	41.9	-8.5894	34.2	-8.2581	26.7
974	ľ	1_	_	55.9	-10.503	54.8	-10.2787	53.2	-10.0615	51.1	-9.645	45.8	-9.2481	39.3		32.2	-8.4965	25.3
1001		4	┺-	52.3	L	51.4	-9.7281	49.9	-9.6112	48	-9.3517	43.1	-9.067	37.1	-8.7649	30.5	-8.4505	24
1035	L		Ŀ	48.7	-9.9332	47.9	-9.7875	46.7	-9.6417	45	-9.3476	40.5	-9.0484	35	-8.743	28.9	-8.431	22.9
1065		1146,435	-8.7555	45.2	-8.7674	44.6	-8.7598	43.6	-8.7348	42.1	-8.6396	38.2	-8.4946	33.2	-8.3096	27.6	-8.0922	22
1096	1.4539	1191.507	-8.9984	41.9	-8.9057	41.4	-8.8144	40.5		39.3	-8.5366	35.8	-8.3402	31.4		26.4	-7.9051	21.2
1127	7 1.488	1237.636	1 -8.5867	38.9	-8.5339	38.4	-8.4745	37.6		36.5	-8.2607	33.5		29.5		25.1	-7.6952	20.4
1155	5 1.4557	57 1278.395	8.8657	36.4	-8.7523	35.9	-8.6412	35.2	-8.5316	34.2	-8.3139	31.5	-8.0943	27.9	7.8695	23.9	-7.637	19.6

1 Year Half Life

1186	1.3568	1320.454	-8.7151	33.8	-8.6247	33.4		32.8	-8.4343	31.9	-8.2323	29.4	-8.0198	26.2	-7.7971	22.5	-7.5642	18.6
1216	1.1416	1354.702	-9.72	31.7	-9.5022	31.3		30.7	-9.1029	29.8	-8.7401	27.6	-8.4028	24.6	-8.0826	21.2	-7.7731	17.7
1247	0.8976	1382.526	-9.6843	29.7	-9.5231	29.3		28.7	-9.1979	27.9	-8.8725	25.8	-8.5492	23.1	-8.2283	19.9	9606.7-	16.7
1277	0.7503	1405.034	-10.1212	27.9	-9.9172	27.5	-9.7187	26.9	-9.5249	26.2	-9.1493	24.2	-8.7864	21.7	-8.4328	18.8	-8.086	15.8
1308	0.6065	1423.837	-10.4139	26.1	-10.2039	25.8	9.9978	25.3	-9.7952	24.6	-9.3997	22.7	-9.0153	20.4	-8.6401	17.7	-8.272	14.9
1339	0.4754	1438 574	-10.8587	24.6	-10,6176	24.2	-10.385	23.7	-10.1581	23.1	-9.7194	21.3	-9.2978	19.1	-8.8897	16.6	-8.4924	14
1369	0.3627	1449 454	-11.1477	23.2	-10.9051	22.8	-10.6673	22.3	-10.434	21.7	9626.6-	20.1	-9.5399	18	-9.1128	15.6	-8.696	13.2
1400	0.2813	1458.174	11,3858	21.8	-11.1418	21.5	-10.9016	21	-10.6651	20.4	-10.2024	18.9	-9.752	16.9	-9.3125	14.7	-8.8822	12.4
1430	0.2573	1465.894	-11.118	20.6	7		-10.7422	19.8	-10.5483	19.3	-10.1525	17.8	-9.7498	15.9	-9.3435	13.8	-8.9356	11.7
1461	0.3486	1476.699	-10,0045	19.3		19	-9.8759	18.7	-9.7871	18.1	-9.5694	16.8	-9.3086	15.1	-9.0144	13.1	-8.6947	11.1
1492	0.4691	1491 242	-9.7482	18	-9.6599	17.8	-9.5661	17.5	-9.4665	17	-9.2489	15.8	-9.0068	14.2	-8.7414	12.5	-8.4545	10.6
1521	0.445	1504 148	-10.623	16.9	١.		-10.1845	16.4	-9.981	16	-9.5959	14.9	-9.2302	13.5	-8.875	11.8	-8.5239	10.1
1552	0.4021	1516,614	-9.8784	15.8		15.7	6929-6-	15.4	-9.5606	15	-9.3044	4	-9.024	12.7	-8.7252	11.1	-8.4119	9.5
1582	0.5174	1532 137	-8.4621	14.8	_	14.7	-8.5114	14.4	-8.507	14.1	-8.4479	13.2	-8.3312	12	-8.1666	10.6	-7.9624	9.1
1613	0 5955		-9.0107	13.8		13.7	-8.7838	13.5	-8.6761	13.2	-8.4642	12.4	-8.2497	11.3	-8.0262	10.1	7.7897	8.7
1643	0.5279		-9,3869	12.9	<u> </u>	12.8	-9.0831	12.6	-8.9364	12.3	-8.6504	11.6	-8.3701	10.6	-8.0913	9.5	-7.8107	8.2
1674	0.406		-10.1715	12.1	Ľ			11.8	-9.5114	11.6	-9.1128	10.9	-8.7374	9	-8.3785	8.9	-8.0309	7.8
1705	0.2864	1	-10,6207	11.4	,	11.3	-10.1488	11.1	-9.9224	10.8	-9.4867	10.2	-9.0705	9.4	-8.6701	8.4	-8.2823	7.3
1735	0 247	1595.31	-10,1358	10.7	-9.9939	10.6	-9.8441	10.4	-9.6878	10.2	-9.3606	9.6	-9.0199	8.8	-8.6708	7.9	-8.3164	6.9
1766	0 2245	1602 268	-10.765		-10,5307	10	Ľ	9.8	Ľ	9.6	-9.6635	6	-9.2571	8.3	-8.8615	7.4	-8.4732	6.5
1796	0.244		-9.4007		İ		_	9.2		6	-9.0521	8.5	-8.8172	7.8	-8.5482	7	-8.2539	6.1
1827	0 202		-9 5956	6			L	8.7	ľ.	8.5	-8.9624	8	-8.6962	7.4	-8.4179	9.9	-8.1266	5.8
1858	0.348	- 1	.8 8915	83	ļ_		L	8.1	L	8	-8.5452	7.5	-8.3485	7	-8.1257	6.3	-7.8802	5.5
1886	0 3397	- 1	-8 9321	7.8	Ľ		Ĺ	7.6		7.5	-8.4329	7.1	-8.2147	9.9	-7.9827	9	-7.7361	5.3
1917	0.3657	1649 347	-8.047	7.3		7.2	-8.0171	7.2	-7.9848	7	-7.8895	6.7	-7.7585	6.2	-7.5964	9.6	-7.4071	2
1947	0.3807	1660.767	-8.3593	6.8	1	9.9	Ľ		L	9.9	-7.8853	6.3	7.6927	5.8	-7.4914	5.3	-7.2787	4.7
1978	0.3614	١.,	-8.1557	6.4				6.3	-7.9244	6.2	-7.7525	5.9	-7.5674	5.5	-7.3696	5	-7.159	4.5
2008	0.3284		-8.6159	9				5.9		5.8	-7.9555	5.5	-7.7061	5.2		4.7	-7.2091	4.2
2039	0.2624	ł	-9 3344	5.6			3 -8.9397	5.5	-8.754	5.4	-8.4017	5.2	-8.069	4.8	-7.7504	4.4	-7.4414	4
2070	0.2129	1	_	5.3			-8.9595	5.2	-8.8061	5.1	-8.4971	4.8	-8.1874	4.5	-7.878	4.2	-7.569	3.7
2100	0.1748	1701.8	Γ.	5	-9.7713	4.9	9-9.549	4.9	-9.3352	8.4	-8.9286	4.6	-8.5441	4.3	-8.176	3.9	-7.8197	3.5
2131	0.1402	-	1	4.7	-9.8229	4.6	9.6359	4.6	-9.4492	4.5		4.3		4		3.7	7.9887	3.3
2161	0.1596	-	-8.641	4.4	-8.6307	4.3	3 -8.6002	4.3	-8.5518	4.2	-8.4101	4	-8.2206	3.8		3.5	-7.7411	3.1
2192	0.1826	1	Ľ	4.1	-8.9655		-8.8356	4	-8.708	4	-8.4556	3.8		3.6		3.3	-7.671	6
2223	0.1715	1721.911	-9.1014	3.8	-8.9764	3.8	3 -8.85		-8.7224	3.7	-8.4635	3.6		3.3		3.1	-7.6514	2.8
2251	0.1504	1726.121	-9.5986	3.6	-9.4127		9.233	3.6	-9.0584	3.5	_	3.4		3.2	-8.0775	2.9	-7.7625	2.6
2282	0.1287	1730.11	-9.5628	3.4	-9.4099	3.4	-9.2555	3.3	-9.1001	3.3	-8.787	3.2	-8.472	3		2.7	-7.8375	2.5
2312	0.1257	1733.88	-9.1692	3.2	-9.068	3.2	8.9599	3.2	-8.8458	3.1	-8.6016	3		2.8		2.6	-7.772	2.4
2343	0.1116	1737.338	-10.0834	3	-9.8549		3 -9.6378	3	-9.4303	2.9	-9.0378	2.8	Ì	2.6	-8.3108	2.4	-7.9633	2.2
2373	0.0873	_	1_	2.8	-9.9864		9 -9.7924	2.8	6665.6-	2.7	Ė	2.6		2.5	-8.4794	2.3	-8.1171	2.1
2404	0.0719	1742.187	-10.4801	2.7	-10.2661		8 -10.0559	2.6		2.6	Ĺ	2.5		2.3		2.2	-8.2825	2
2435	0.0686	\bot	-9.9727	2.5	-9.8442			2.5	-9.5636	2.4		2.3		2.2		7	-8.2617	1.9
2465	0.064	↓_	-10.653	2.4	-10.4205		3 -10.197	2.3	19:381	2.3	-9.5662	2.2	-9.1679	2.1	-8.7801	1.9	-8.399	1.7
2496	0.0618	1748.15	_	2.2	-9.7549	3 2.2	2 -9.6427	2.2	-9.52	2.2		2.1	Ĺ	1.9		6 .	-8.3081	1.6
2526	0.0684	1750.142	19.8997	2.1	-9.8466		1 -9.694	2.1	-9.5411	2		1.9	-8.9182	1.8		1.7	-8.2678	1.6
2557	0.0576	1751.929	-10.5783	2	'		2 -10.1408	1.9	9.9322	1.9		1.8	-9.1429	1.7	-8.7652	1.6	-8.393	1.5
2588	0.0551	1753.638	9.7279	1.8	9.6398	3 1.8	8 -9.5386	3.	-9.4261	1.8	-9.1737	1.7	-8.8931	1.6	-8.5914	1.5	-8.2737	4.

1 Year Half Life

1.3	1.2	1.2	1.1	1.1	-	0.9	6.0	0.8	0.8	0.7	0.7	0.7	9.0	9.0	9.0	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
-8.1882	-8.0326	-7.9157	-7.811	-7.7912	-7.9385	-8.0943	-8.1911	-8.2224	-8.0285	-7.9082	-7.7662	-7.6472	-7.5392	-7.2921	-7.477	-7.5639	-7.727.7	-7.9445	-8.0674	-8.0874	-7.9282	-7.6939	-7.33	7.0607	-6.9025	-6.8877	-6.9515	-6.9621	-7.1567	-7.2961	-7.5739	-7.781	-8.0031	-7.9968	-7.933	-7.8301	-7.9744	-8.128	-7.6949	-7.3307	-7.4202	-7.7067	-7.9505	-7.9186	-7.5996	-7.4909
1.4	4.	1.3	1.2	1.1	1.1	-	-	6.0	8.0	9.0	0.8	0.7	0.7	9.0	9.0	9.0	0.5	0.5	0.5	9.0	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
-8.4976	-8.3147	-8.1921	-8.0818	-8.0773	-8.2729	-8.4513	-8.5492	-8.5692	-8.3102	-8.1866	-8.0273	-7.9004	-7.7874	-7.4936	-7.7723	-7.8605	-8.0549	-8.3045	-8.4242	-8.4231	-8.2097	-7.9342	-7.5112	-7.2285	-7.084	-7.0981	-7.1876	-7.1944	-7.439	-7.5856	-7.9155	-8.1308	-8.3766	-8.324	-8.2356	-8.1092	-8.3119	-8.4887	-7.9058	-7.5078	-7.687	-8.0473	-8.318	-8.2321	-7.8214	-7.7338
1.5	1.5	4	1.3	1.2	1.1	1.1	-	-	6.0	0.8	0.8	0.8	0.7	0.7	9.0	9.0	9.0	0.5	0.5	0.5	4.0	4.0	0.4	4.0	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
-8.7956	-8.5804	-8.4555	-8.3404	-8.3573	-8.6131	-8.8135	-8.9081	-8.912	-8.5702	-8.4523	-8.2734	-8.1399	-8.0231	-7.6722	-8.077	-8.1556	-8.387	-8.6733	-8.7827	-8.7531	-8.4722	-8.1529	-7.6635	-7.3746	-7.2524	-7.303	-7.4216	-7.4199	-7.7276	-7.8761	-8.2699	-8.4868	-8.7597	-8.6421	-8.5272	-8.3744	-8.6559	-8.8549	-8.0763	-7.6574	-7.958	-8.4021	-8.6961	-8.5343	-8.0128	-7.9662
1.6	1.5	4.	1.4	1.3	1.2		1.	-	6.0	6.0	0.8	9.0	0.7	0.7	0.7	9.0	9.0	0.5	0.5	0.5	0.5	0.4	4.0	4.0	0.4	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.7	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	1.0	0.1	0.1	0.1	0.1
-9 082	-8.8277	-8.7059	-8.5867	-8.6326	-8.963	-9.1825	-9.2679	-9.2499	-8.8031	-8.7059	-8.5033	-8.3656	-8.2464	-7.8249	-8.3989	-8.4487	-8.7268	-9.0539	-9.1427	-9.0759	-8.7116	-8.3477	-7.7834	-7.4991	-7.4092	-7.5046	-7.6551	-7.6385	-8.0265	-8.168	-8.6418	-8.8499	-9.1547	-8.9472	-8.8064	-8.6239	-9.0114	-9.2284	-8.1944	-7.7792	-8.2404	-8.7769	-9.087	-8.8207	-8.1671	-8.191
171	1.6	1.5	1.4	1.3	1.2	1.2	=	-	-	6.0	6.0	0.8	0.8	0.7	0.7	9.0	9.0	9.0	0.5	0.5	0.5	4.0	4.0	4.0	4.0	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
-9 3573	-9.0541	-8.9435	-8.8204	-8.9052	-9.3278	-9.5601	-9.6284	-9.5817	-9.002	-8.9487	-8.7158	-8.5772	-8.4572	-7.9477	-8.7482	-8.738	-9.0777	-9.4497	-9,5033	-9.3892	-8.9225	-8.516	-7.8675	-7.6031	-7.5565	-7.7056	-7.8903	-7.8494	-8.3408	-8.4613	-9.0371	-9.22	-9.5647	-9.2336	-9.0717	-8.8558	-9.3857	9.6109	-8.2444	-7.8748	-8.5435	-9.1779	-9.4927	-9.0846	-8.2767	-8.4125
171	1.6	1.5	1.4	1.3	1.3	1.2	1.1		-	0.9	0.9	0.8	0.8	0.7	0.7	9.0	9.0	9.0	0.5	0.5	0.5	4.0	4.0	4.0	4.0	4.0	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
.9 4913	-9.1585	-9.0577	-8.9324	-9.0413	-9.5177	-9.7526	-9.8086	-9.7448	-9.0859	-9.067	-8.8148	-8.6778	-8.5579	-7.9964	-8.9374	-8.8803	-9.2587	-9.6544	-9.6833	-9.5414	-9.0152	-8.5896	-7.8947	-7.648	-7.6273	-7.8068	-8.0092	-7.9516	-8.5057	-8.6081	-9.2459	-9.4074	-9.7764	-9.3673	-9.1987	-8.9644	-9.5827	-9.8059	-8.2377	-7.9139	-8.7067	-9.3905	-9.7016	-9.2052	-8.3118	-8.5241
17	1.6	1.5	4.	4.1	1.3	1.2	Ξ	-	1	6.0	6.0	8.0	0.8	0.7	0.7	0.7	9.0	9.0	0.5	0.5	0.5	0.5	4.0	4.0	0.4	4.0	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1
CECA 9.	-9.2565	-9.1692	-9.0413	-9.1778	-9.7139	-9.9478	-9.9887	-9.9056	-9.1579	-9.1838	-8.9088	-8.7749	-8.6555	-8.0358	-9.1391	-9.02	-9.4442	-9.8643	-9.8625	-9.6901	-9.0982	-8.6558	-7.9115	-7.6886	-7.6968	-7.9091	-8.1293	-8.0513	-8.6771	-8.7549	-9.4636	-9.5962	-9.9933	-9.4931	-9.3218	-9.0678	-9.7882	-10.0035	-8.2061	-7.9484	-8.8799	-9.6126	-9.9145	-9.3166	-8.3324	-8.6378
171	1.6	1.5	4.	4.1	1.3	1.2	=	-	-	6.0	60	0.8	0.8	0.7	0.7	0.7	9.0	90	0.5	0.5	0.5	0.5	4.0	4.0	4.0	0.4	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	1.0	0.1	0.1
0 7530	-9.3474	-9 278	-9.1469	-9.3151	-9.9174	-10.1457	-10,1683	-10.0639	9 2 1 6 5	-93	-8 9973	-8 8686	-8.7501	-8.0649	-9.3559	-9.1561	-9.6351	-10.08	-10.0406	-9 8347	-9.1704	-8 7144	-7.9173	.7.7255	-7.7654	-8.0129	-8.2508	-8.1483	-8.8561	-8.9012	-9.6916	-9.7858	-10.216	-9.6093	-9.4411	-9.1655	-10.0041	-10.2037	-8.1461	-7.9795	-9.0653	-9.845	-10.1316	-9.4168	-8.3372	-8.7549
1765 336	1757 304	1759 278	1761 299	1763.151	1764.757	-	╀-	↓_	+-	1770.442	1771 727	1772 947	1774 234	1775.541	1776.758	1777 696	1778 524	1779 184	1779 719	1780 251	1780 823	1781511	1782.313	1783.119	1784.006	1784.794	1785.506	1786.129	1786.686	1787 15	1787.515	1787.813	1788.051	1788.285	1788.541	1788.787			1	1789 741	1790.027	1790.234		1	1	1790.884
1 9090 0	-	4	1		1	_	₩	٠.	4	-	+-		┸		т.	4-	\perp	٠.	- 1	1	1	+-	+	0.0288	0.0286	0.0263	.1	1	0.018	0.015	0.0122	9600.0	0.0079	0.0075	0.0082	0.0088	0.0079	0 0062	0.0074	86000	0.0092	0.0067	0.0048	0.0045	0.0057	0.0063
2646	2647	2677	2708	2738	2769	2800	2830	2861	2891	2922	2053	2982	3013	3043	3074	3104	3135	3166	3196	7000	3257	3288	3319	3347	3378	3408	3439	3469	3500	3531	3561	3592	3622	3653	3684	3712	3743	3773	3804	3834	3865	3896	3926	3957	3987	4018

Amendments

ute Mass Flux	-		•	ı		-	A								
		Node 8	_	Node 11	-	Node 14	_	Node 17		Node 20		Node 23		Node 26	
	mdd	(meters)) mdd	(meters)	mdd (meters)	mdd									
	8	-14.5	1400	-14.25	0	-14	0	-13.5	0	-13	0	-12.5	0	-12	0
İ	1408	-14.4038	1272.6	-14.1614	118.7	-13.9267	-17.3	-13.4497	4.4	-12.9654	-1.1	-12.4762	0.3	-11.9837	0
	1385.9	-14.3397	1118.5	-14.0986	273.9	-13.868	-19.7	-13.4002	4.2	-12.925	-0.9	-12.444	0.2	-11.9584	0
	1339.7	-14.2904	1026.5	-14.0498	362.4	-13.8209	4.6	-13.3574	-2.4	-12.8872	0.8	-12.4114	-0.2	-11.9308	0
0	1290.7	-14.2496	969.2	-14.0092	411.3	-13.7812	39.6	-13.3202	-9.8	-12.8531	2.4	-12.3807	-0.5	-11.9036	0.1
0.0001	1244.7	-14.2142	929.5	-13.974	440	-13.7466	76.1	-13.2872	-15.2	-12.8223	8	-12.3523	9.0-	-11.8778	0.1
0.0001	1194.5	-14.1773	893.9	-13.9373	461	-13.7103	116.5	-13.2523	-18	-12.7892	2.5	-12.3213	-0.3	-11.8492	0
-0.0003	943.3	-13.6827	759	-13.4558	518.6	-13.2585	286.7	-12.8541	27.5	-12.438	-3.1	-12.0115	0.5	-11.5761	0
0.0021	723.8	-13.247	635.7	-13.0262	505.6	-12.8432	362.8	-12.468	126.3	-12.0812	20.7	-11.6839	1.5	-11.2768	0.1
0.0302	593.9	-13.1689	539.9	-12.9431	459.2	-12.7494	363.5	-12.3579	180	-11.9605	61.2	-11.5573	13.2	-11.1483	1.3
0.1488	507.8	-13.1464	470.1	-12.9185	412.6	-12.7201	343.1	-12.3203	199.3	-11.9164	89.5	-11.5082	29.8	-11.0957	5.2
0.3741	447.4	1	418.6	-12.9959	374.4	-12.7891	319.9	-12.3745	202.7	-11.9578	104.8	-11.5388	42.7	-11.1173	10.7
0.6127	408	1	382.2	-13.473	343.6	-13.232	296.7	-12.7558	195.2	-12.2859	107.8	-11.8209	48.3	-11.3594	14.8
0.7658	382.1	-13,9597	356.4	-13.7115	319.4	-13.467	276.1	-12.9813	183.6	-12.4994	103.9	-12.0207	48.2	-11.5446	16.5
0 9092	354.9	i i	332.1	-13.6153	299	-13.3887	259.5	-12.9331	175.1	-12.4747	101.4	-12.0142	48.7	-11,5519	17.7
1 0942	325.3	1	306.7	-13.634	278.4	-13.4054	243.7	-12.9473	168.1	-12.488	100.1	-12.0272	50.2	-11.5651	19.3
1.4861	289.8		276.7	-12.8199	255.6	-12.6543	228.2	-12.3077	164.6	-11.9434	103.4	-11.5637	55.7	-11.1709	23.3
2 1376	257.8	1	247.8	-13.084	231.6	-12.873	210.4	-12.4521	158.7	-12.0313	105.7	-11.6093	61.2	-11.1852	28.7
2.6591	237.4		228	-13.3821	213.4	-13.1519	194.6	-12.6943	149.2	-12.2397	102.1	-11.7872	61.3	-11,3359	31.2
3.164	218.8	1	210.9	-13.0259	198.3	-12.8326	181.9	-12.4382	141.7	-12.0345	99.3	-11.623	61.7	-11.2048	33
3.8608	198.9		192.5	-13.1029	182.1	-12.8939	168.3	-12.4745	134	-12.0529	9.96	-11,6288	62.4	-11.2019	35.3
4.3994	184.6	1	178.6	-13.4623	169.1	-13.2264	156.6	-12.7588	125.8	-12.2955	92.1		6.09	-11.3775	35.9
4.7667	172.7	-13.876	166.8	-13.6309	157.8	-13.3934	146.2	-12.9202	117.9	-12.449	87	-11.9795	58.1	-11.5113	35.3
5.1273	160.7	-13.6908	155.6	-13.4552	147.5	-13.2388	137	-12.8018	111.2		82.8		56.2	-11.4649	34.7
5.4611	149.7	-14.0129	145.1	-13.7647	137.7	-13.5208	128.2	-13.0367	104.6		78.6		54	-11.604	34
5.7202	140	-13.9255	135.7	-13.6846	128.9	-13.4559	120.1	-12.9965	98.3	-12.5346	74.3		51.5	-11.6053	32.9
6.1063	129.5		125.9	-13.3079	120.2	-13.1076	112.5	-12.6992	93	-12.2815	71.1	-11.8558	50.2	-11.4231	32.5
6.6568	118.8	-13.4365	115.9	-13.2059	111.1	-13.0013	104.5	-12.5882	9.78	1	68.2		49.2	-11.3186	32.5
7.38	108.8	-12.909	106.4	-12.6937	102.4	-12.5222	6.96	-12.1684	82.4		65.4		48.3	-11.0346	32.9
8.187	99.7	-13.2231	97.6	-12.9892	94.2		89.5	-12.3582	77.1		62.2		47	-11.0979	33
8.9819	91.7	-12.8739	6.68	-12.6544	86.9	-12.4738	82.8	-12.1048	71.9	-11.7265	58.9		45.3	-10.9463	32.7
9.9709	84.1	-12.2787	82.6	-12.0751	80.1	-11.9285	7.97	-11.6225	9.79	-11.3009	56.3		44.3	-10.6167	32.8
11.1344	76.8	-12.628	75.5	-12.4031	73.4	-12.2119	5.07	-11.8305	62.8		53.1		42.7	-10.681	32.5
11.9472	71.4	-13.1153	70.1	-12.877	68.1	-12.6563	65.5	-12.2198	58.5	-11.7883	49.9		40.4	-10.9348	31.3
12.6236	66.3	-12.9854	65.1	-12.7581	63.4	-12.5603	60.9		54.6		46.8		38.3	-10.935	30
13.1243	61.9	-13.5247	6.09	-13.2781	2.65	-13.0385	57	-12.5657	51.2	-12.0997	44	_1	36.2	-11.1815	28.6
13.4534	58.1	-13.5649	57.1	-13.324	55.5	-13.0957	53.4	-12.6388	48	-12.1816	41.3	-11.7241	34.1	-11.2663	27.1
13.6873	54.5	-13.824	53.6	-13.5764	52.1	-13.3323	50.1	-12.8473	45	-12.3656	38.9	-11,8866	32.1		25.7
13.9406	51.1	-13.387	50.2	-13.1582	48.9	-12.9546	47.1	-12.5392	42.4	-12.1145	36.7	-11.682	30.5		24.4
14.2731	47.6	-13.4241	46.9	-13.1875	45.7	-12.9692	44.1	-12.5311	39.9	-12.0906	34.7	-11.6474	29	-11.2014	23.3
14.7068	44.2	-12.7259	43.6	-12.5117	42.6	-12.342	41.2	-11,9894	37.5	-11.6213	32.8	-11.2397	27.7	-10.8462	22.4
15.2453	40.9	-12.823	40.4	-12.5948	39.6	-12.3957	38.4	-11,9954	35.1	-11.592	31	-11.1845	26.4	-10.7727	21.6
15.7621	38	-12.6039	37.5	-12.3818	36.8	-12.195	35.7	-11.8155		-11.4285	29.1	-11.0345	25	-10.6338	20.6
16.2023	35.5	Ľ	35.1	-12.5081	34.4		33.5	!	30.9		27.6		23.7	-10.6463	19.8
16.6349	33.1	-12.65		-12.4256	32.1	_	31.2		28.9		25.9		22.4	-10.5952	18.8
16.9443	31	-13.1479	30.7	-12.902	30.1	-12.6637	29.3	-12.1926	27.1	-11.7273	24.3	-11.2662	21.1	-10.8078	17.8

Amendments

16.8	15.9	15	14.2	13.4	12.6	11.9	11.3	10.8	10.2	9.7	9.2	8.8	8.3	7.8	7.3	6.9	9.9	6.2	5.9	5.6	5.3	5	4.7	4.5	4.2	4	3.7	3.5	3.3	3.2	3	2.8	2.7	2.5	2.4	2.2	2.1	2	1.9	1.8	1.7	1.6	1.5	1.4	1.3	1.3	1.2	-
-10.8412	-10.9295	-10.9954	-11.0843	-11.1444	-11.1885	-11.1206	-10.8263	-10.6653	-10.8111	-10.6732	-10.2878	-10.2995	-10.3882	-10.5889	-10.7291	-10.6352	-10.7269	-10.4181	-10.3545	-10.16	-10.113	-9.8833	-9.8944	-9.8465	-9.9403	-10.1282	-10.1431	-10.2936	-10.3099	-9.9738	-9.9676	-9.9522	-10.0471	-10.05	-9.9437	-10.111	-10.1604	-10.2219	-10.1062	-10.2113	-10.0459	-10.0206	-10.1324	-9.9608	-9.9153	-9.8111	-9.7708	-9.7332
	_	- 17.7	16.7	15.7	14.8	4	13.3	12.6	11.9	11.2	10.7	10.1	9.5						6.7	6.3	9	5.6	5.3	5	4.7	4.4	4.2		L	3.5	3.3	3.1	2.9	2.8	2.6	2.5	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	1.5	1.4	1.3	1.2
-11.2941	-11.3968	-11.4701	-11.5716	-11.6371	-11.6837	-11.5991	-11.2589	-11.0932	-11.2792	-11.1112	-10.6728	-10.7182	-10.8273	-11.0594	-11.2129	-11.0944	-11.2091	-10.8435	-10.7921	-10.5733	-10.5332	-10.2731	-10.3049	-10.2535	-10.3696	-10.5859	-10.5935	-10.7703	-10.7804	-10.3862	-10.4029	-10.3895	-10.5044	-10.5033	-10.3799	-10.5833	-10.6321	-10.7005	-10.5612	-10.6916	-10.4925	-10.4743	-10.6086	-10.4021	-10.3598	-10.2425	-10.2032	-10.1639
22.9		20.3	19.1	18	17	16	15.1	14.3	13.5	12.7	12	11.3	10.6	10	9.4	8.8	8.3	6.7	7.4	7	9.9	6.2	5.8	5.5	5.1	4.8	4.5	4.3	4	3.8	3.6	3.4	3.2	3	2.8	2.6	2.5	2.4	2.2	2.1	2	1.9	1.8	1.6	1.6	1.5	4.	1.3
-11.7454	-11.8646	-11.945	-12.0601	-12.1306	-12.1794	-12.075	-11.6825	-11.5152	-11.7494	-11.5434	-11.0453	-11.1342	-11.2657	-11.5326	-11.6986	-11.5495	-11.6925	-11.2589	-11.2261	-10.9792	-10.9492	-10.6539	-10.7122	-10.6555	-10.7976	-11.0453	-11.0416	-11.2489	-11.2497							-11.0577	-11.1033	-11.1793	-11.0115	-11.1732	-10.9332	-10.9256	-11.086	-10.8372				-10.5908
25.4	23.9	22.5	21.2	20	18.9	17.8	16.8	15.8	14.9	14	13.1	12.3	11.5	10.8	10.2	9.6	6	8.5	80	7.5	7.1	9.9	6.2	5.8	5.5	5.1	4.8	4.6	4.3	4	3.8	3.6	3.4	3.2	3	2.8	2.6	2.5	2.3	2.2	2.1	2	1.8	1.7	1.6	1.5	1.5	1.4
-12.1949	-12.3333	-12.4203	-12.5503	-12.6252	-12.6759	-12.5477	-12.0955	-11.9311	-12.223	-11.9689	-11.4037	-11.5486	-11.7038	-12.0093	-12.1867	-11.9998	-12.1778	-11.6626	-11.6568	-11.3768	-11,3612	-11.0248	-11.1167	-11.0525	-11.2251	-11.507	-11.4873	-11.7303	-11.7175	-11.1769	-11.2664	-11.2546	-11.42		-11.2363	-11.5352	-11.574	-11.6584	-11.4566	-11,6569	-11.3669	-11,3745	-11,5651	-11.265	-11,239	-11.0893	\sqcup	-11.0138
27.5	25.8	24.3	22.9	21.6	20.3	19.2	18	16.9	15.9	14.9	4	13.1	12.2	11.5	10.8	10.2	9.6	6	8.5	7.9	7.5	7	6.5	6.1	5.7	5.4	5.1	4.8	4.5	4.2	4	3.7	3.5	3.3	3.1	2.9	2.8	2.6	2.4	2.3	2.2	2	1.9	1.8	1.7	1.6	1.5	1.4
-12.6424	-12.8034	-12.8962	-13.0427	-13.1211	-13.1733	-13.0167	-12.4964	-12.3407	-12.7013	-12.3866	-11.7463	-11.9625	-12.1424	-12.4907	-12.6775	-12.4442	-12.6658	-12.0523	-12.0847	-11.7654	-11.7695	-11.3848	-11.5192	-11.4443	-11.6527	-11.9722	-11.9303	-12.2154	-12.1836	-11.5513	-11.696	-11.6825	-11.8796	-11.8489	-11.6555	-12.017	-12.044	-12.138	-11.8957	-12.1437	-11.7925	-11.8213	-12.0466	-11.6841	-11.6737	-11.504		-11.4328
28.2	26.5	24.9	23.5	22.2	20.9	19.7	18.5	17.3	16.3	15.3	14.3	13.3	12.5	11.7	Ξ	10.4	8.6	9.2	9.8	1.8	7.6	7.1	9.9	6.2	5.8	5.5	5.1	4.8	4.6	4.3	4	3.8	3.6	3.3	3.2	3	2.8	2.6	2.5	2.3	2.2	2.1	1.9	1.8	1.7	1.6	1.5	4.1
-12.8652	-13.0392	-13.1344	-13.2898	-13.3696	-13.4223	-13.2495	-12.6917	-12.5431	-12.9429	-12.5919	-11.911	-12.1697	-12.362	-12.7336	-12.9242	-12.6638	-12.9112	-12.2411	-12.2978	-11.9559	-11.9723	-11.5604	-11.7199	-11.6381	-11.8669	-12.2064	-12.1506	-12.4598	-12.4159	-11.7323	-11.9107	-11.8952	-12.1102	-12.0709	-11.8625	-12.2601	-12.2787	-12.3782	-12.1125	-12.3886	-12.0017	-12.0441	-12.2887	-11.89	-11.89	-11.7089		-11.6407
28.8	27.1	25.4	23.9	22.6	21.3	20.1	18.9	17.6	16.6	15.5	14.5	13.5	12.7	11.9	11.2	10.6	6.6	9.3	8.7	8.2	7.7	7.2	6.7	6.3	5.9	5.5	5.2	4.9	4.6	4.3	4.1	3.8	3.6	3.4	3.2	9	2.8	2.7	2.5	2.4	2.2	2.1	2	1.8	1.7	1.6	1.5	4
-13.1034	-13.2836	-13.3796	-13.5389	-13.6191	-13.672	-13.4918	-12.9171	-12.7722	-13.1902	-12.822	-12.1221	-12.4013	-12.5991	-12.9813	-13.1731	-12.9002	-13.1597	-12.4631	-12.5318	-12.179	-12.2015	-11,7763	1	ł	1			1	L.	1 .	-12.1453	-12.1286				Ľ	-12.522	Ľ	-12.3474	<u> </u>		-			1_	-11.9384		-11.8717
29.1	27.4	25.7	24.2	22.9	21.6	50.4	19.1	17.8	16.7	15.7	14.6	13.6	12.8	12	11.3	10.7	10	9.4	8.8	8.2	7.8	7.2	6.8	6.3	5.9	5.6	5.2	4.9	4.6	4.4	4.1	3.8	3.6	3.4	3.2	3	2.8	2.7	2.5	2.4	2.2	2.1	2	1.9	1.8	1.6	1.6	1.5
17.1597	17.3306	17.4541	17.5322	17.5726	17.5969	17.6356	17.7563	17.945	18.0809	18 2054	18 4109	18 6457	18.8109	18.9171	18.9713	19.0247	19.0772	19.1498	19.2563	19.3708	19 4826	19 6184	19.7521	19.8738	19.9744	20.0442	20.0965	20.1343	20.1612	20.2096	20.2732	20.326	20.3641	20.3978	20.4344	20.4649	20.4829	20.4978	20.5155	20.5315	20.549	20.5704	1_	20.6027	20.6222	20.645		20.691
0.0069	0.0057	0.004	0.0025	0.0013	0.0008	0.0013	0.0039	0.0061	0 0047	0 004	0 008	0 0076	0.0055	0.0034	0.0017	0.0018	0.0017	0.0024	0.0034	0.0037	0 004	0 0044	0 0045	0.0039	0.0034	0.0022	0.0017	0.0013	0.000	0.0016	0.002	0.0017	0.0014	0.0011	0.0012	0.001	9000.0	0.0005	0.0006	0.0005	0.0006	0.0007	0.0005	0.0005	0.0007	0.0007	0.0008	0.0007
1247	1277	1308	1339	1369	1400	1430	1461	1492	1521	1552	1582	1613	1643	1674	1705	1735	1766	1796	1827	1858	1886	1917	1947	1978	2008	2039	2070	2100	2131	2161	2192	2223	2251	2282	2312	2343	2373	2404	2435	2465	2496	2526	2557	2588	2616	2647	2677	2708

Amendments

7
2001-01-
1.1 -10.9279 1
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1.1
1.1 -12.0103
.1 -12.3271
20.7438 1.1
0.0003 20.

138 8				0.25		0.5		0.75		1		1.5		2	1 1	2.5	1 1	3
Time	Solute Ma	s Flux	Node 5		Node 8		Node 11	_	Node 14	_	Node 17		Node 20		Node 23		9	
(Davs)		(grams)	S)	Mdd	(meters)	ЬРМ	(meters)) Мдд	(meters)	PPM ((meters)) Mdd	(meters)	Mdd	(meters)	PPM	(meters) P	PPM
0	0		-14.75	1400		1400	-14.25	0	-14	0	-13.5	0	-13	0	-12.5	0	-12	0
5	0	0	-15.5229	1442.8	-15,2269	835.8	-14.9247	400.6	-14.5562	10.2	-13.8798	-1.9	-13.2605	0.4	-12.6789	-0.1	-12.1222	0
9	0	-0.0001	-15.4185	1268.6	-15.1534	879.8	-14.8818	472.2	-14.5722	136.6	-13.9598	-17.5	-13,3621	2.6	-12.7812	4.0-	-12.216	0
15		0	-15.2353	1235.6	7	836.4	-14.7286	468.6	-14.458	175.5	-13.9078	-11.7	-13.3526	-0.2		0.3		0
20		0.0001	-15.1178	1228.8	٦	831.1	-14.6196	453.4	-14.3632	184	-13.8417	-6.8	-13.3126	-1.7	_	9.0		-0.1
25		0.0002	-15.0207	1209.3	-14.7755	847.1	-14.5279	445.8	-14.28	182.1	-13.7761	4-	-13.2639	-2.3	-12.7463	0.7	-12.2254	-0.1
31		L	-14.9177	1177	7	851.3	-14.4296	456.9	-14.1889	186	-13.6996	-4.6	-13.2018	-2.1	-12.6975			0
9	0	L		1006.3	-14.375	816.8	-14.1347	512.2	-13.9048	242.5	-13.4391	7.9	-12.9665	-4.2	-12.4879	0.8	-12.0042	-0.1
6		L	_	890	-15.0906	773.6	-14.8234	482.6	-14.527	265.8	-13.9468	27.6	-13.3802	-5.1	-12.8246	0.4	-12.2778	0
12	9	<u> </u>	4-	665.8	7	L		440.2	-15.7772	327.1	-15.0277	123.8	-14.3144	22.9	-13.6313	1.6	-12.9737	0.2
152			4	440.4	1		1	347.2	-17.237	296.7	-16.3247	182.4	-15.4653	83.9	-14.6509	27.6	-13.8753	5.3
187	Ι,		1	329.8	1		L.	282.7	-18.2968	252.8	-17.302	183.1	-16,3614	113.7	-15.4684	58.1	-14.6173	21.1
243	\perp	\perp		248	1		L.	225.8	-19.3	210.2	-18.2192	167.4	-17.1977	118.9	-16.2286	74.5	-15.3059	39.4
244	L	T.	۰	2	17		į	187.1	-19.653	176.3	-18.5951	147.8	-17,5813	113.7	-16.6086	79.9	-15.6743	50.9
27.4	\perp	Τ,				164.7	1_	159	-19.5001	151.8	-18.5172	131	-17.5601	105.4	-16.6293	79.1	-15.7248	55.4
305	1	_	4-	147.2	1_		Ľ,	139.6	-18.4719	133.6	-17.6785	117.1	-16.878	7.96	-16.0763	75.3	-15.2781	55.6
335		4-	1	135.7	1		1_	127.2	-17.0745	121.8	-16.4646	106.9	-15.8277	1.68	-15.171	70.5	-14.5005	53.4
200	l	┵	+		1	123	1	117.7	-16 3955	112.4	-15 7972	7.86	-15.1869	82.4	-14.5668	65.7	-13.9389	50.5
200	\perp	4-			7		1	109	-16 0225	1.42	-15 4202	91.6	-14.8134	76.8	-14.203	61.6	-13.5899	47.8
160		1	+	108.6		L	L	101 7	-15 4233	97.5	-14 8824	85.9	-14 3297	72.2	1		-13.1983	45.4
674	-0.0322	109012- 2				L	ш.	95.3	-14 9874	91.2	-14 4651	803	-13.9346		1		1	42.8
450		- 1	_		1		+	86.6	-16 5141	83.6	-15 7073	748	-14 9436	L	-14.215	52	-13.5148	41
460			+-		1		┸	75.2	-17.8801	73.6	-16.9208	67.6			Γ,	49.5		39.8
547	\perp	-	1		Ľ		1	66.1	-18.7237	64.9	17.7116	9.09			-15.8354	46.4	-14.9607	38.3
278	Ţ,	┿	+-					28	-19.531	57.2	-18.4526	54	<u> </u>	49	-16.4538	42.9	-15.5225	36.2
5	L	4	┷-		1		Ľ.	51.3	-19.7606	50.7	-18.7127	48.2		44.3	3 -16.7344		-15.7998	33.8
639	L	٠.	4-		3 -20.2419	46.2	-19.9172	46.1	-19,4346	45.6	-18.4822	43.6	-17.5489	40.3	3 -16.6365	_	-15.7461	31.4
670		_	+	41.9	1		_	42.1	-18.1821	41.6	-17.4437	39.8	-16.6896	36.9	15.9271	33.2	-15.1618	29
200	\perp		+-		[]		-17,2397	39.2	-16.9494	38.8	-16.3469	36.9	-15.7203	34.2	-15.0755	30.7	-14.4176	27
731			+		1			36.7	-16.3186	36.2	-15.7255	34.4	1_		3 -14.5083	3 28.6	-13.8878	25.1
762	Ľ	1.			١,		I	34.4		8	-15.0029	32.2	-14.4606	3 29.7	-13.9054		L_	23.5
6	┸		_		1		-14.8962	32.6	-14.6798	32.4	-14.2297	30.7	-13.7591	28.1	13.2709		-12.7681	22.1
821	Ι,	╄-	┺-		9 -15.8294	1 29.9	-15.5569	30.4	-15.2465	30.4	-14.6382	28.8	-14.0432	26.4	13.458	3 23.7	-12.8802	20.8
851	1	╀		1 26.7	7 -17.6262	27.1	-17.3006	27.3	-16.8504	27.3	-15.9941	26.5	-15.1875	5 24.7	7 -14.4221		-13.6909	19.6
88		41.3101	1 -18.913	23.9	9 -18.6013	3 24.3	18.2705	24.5	-17.7917	24.5	-16.8717	23.9	-15.9966	3 22.6	5 -15.1611			18.4
912	2 -0.0345	5 -42.3461	1 -20.2257	21.6	6 -19.8876	3 21.9	-19.5317	22.1	-18.9797	22.1	-17.9274	21.6						17.2
943	3 -0.0363	13 -43.4717	7 -20.7353	19.5	5 -20.4059			19.9		19.9	-18.461	19.5		_	-			15.9
974	-0.035	15 -44.5567	7 -21.1665		`		l	18	\perp	18	_	17.7	_					14.6
1001	4 -0.0314	4 -45.4986	6 -20.629				!	16.4		16.4	-18.5817	16.2	_					13.5
1035	5 -0.0247	17 -46.2651	1 -19.417		9 -19.1398	15.1	18.8505	15.2	-18.4736	15.2	-17.7076	14.9			_1			12.5
1065	5 -0.0169	Ľ	7 -17,941	13.8	8 -17.6962		2 -17.4387	14.2	-17.151	14.2	_	13.9	i				1	11.6
1096	6 -0.0107	77 -47.105	5 -17.1873	12.8	•			13.4		13.4		13.1			l	-		10.8
1127	7 -0.0068	Ľ	_	12	2 -16.1731	12.4	4 -15.9247	12.6	-15.6702	12.6	1	12.3	1	11.7	-			10.1
1155	5 -0.0042	┡	3 -16.0363	11.3	3 -15.7908	11.6	3 -15.5409	12	-15.2859	12	-14.7687	11.6	-14.2429	11.1	1 -13.7093		_	9.6
1186	6 -0.0045	15 47.5713	3 -16.5656	3 10.5	5 -16,3001	10.9		11.1	-15.7085	11.2		10.9			_	2.		6
1216	9800:0- 9	38 -47.8361	18.4194			3 9.9			_	10.2			_		_ 1			8.4
1247	7 -0.0129		2 -19.5027		ᆜ					9.2	1		_1		. 1			7.9
1277	7 -0.0143				-1			8.4		8.4	i	8.4	_1		_			7.3
1308	98 -0.0145	45 -49.1154	-21.0039	9 7.4	4 -20.6754	4 7.6	6 -20.3289	7.6	-19.7918	[]	-18.7561		-17.7675	5.7	-16.821/	7,	15,9149	0.7

APPENDIX C.

CLIMATOLOGICAL DATA

STATION NUMBER 353847 ELEMENT: DAILY MEAN TEMPERATURE

QUANTITY: MONTHLY AVERAGE

STATION: Hermiston, Oregon FROM DATA WITH UNITS: DEGREES F

a = 1 day missing, b = 2 days missing, c = 3 days, ..etc.., z = 26 or more days missing, A = Accumulations present Long-term means based on columns; thus, the monthly row may not sum (or average) to the long-term annual

MAXIMUM ALLOWABLE NUMBER OF MISSING DAYS: 9

1984 33.53 1985 28.05	NAL	FEB	MAR	APR	MAY	N O O	JUL	AUG	SEP	- ၁	S S S	חבר	ANN
1985	20 60	000	47.47	50.02	1	63.42		1	60.22	49.23	41.70	29.71	51.12
1985	00.00	100	1 7 7 7	10.00		86.18			57 75	50.92	29.42	22.10	49.21
	28.05	31./3	44.13	04.40		9 6			7 7 0	1000	72.40	20 CE	52 1R
1986	34.31	39.50	49.35	50.78		27.00			24.00	20.05	40.40	32.90	
1087	31.56	39.98	47.90	55.23		67.62			65.68	51.90	43.37	34.95	53.45
000	20.00	40.70	46.06	53.72		65.45			63.52	57.89	46.27	34.19	53.76
006	10.00	9 6	20.0	64.62		200 0000			63.55	52.40	45.52	34.39	51.13a
1989	39.10	20.08	20.1	4.0		700.000			88	50 44	45 33	25.13	53 41
1990	40.61	38.38	45.7	20.00		00.00			0.00	r -		20.00	;
1001	200 000	44 16	200 6666	Z00 6666		200.6666		Ç,	200.6666	3999.00z	9999.00z	9999.00z	44.16K
- 66	200.000	2 000	200.000	56 27		73.03			62.75	54.13	42.77	33.61	59.44c
3 7661	200.688	3999.002	200.000	3 6		BE 47			64 63	54 92	35 12	36.90	51.10
1993	23.98	30.91	42.10	22.03		4.00			2	1 !			
1994	40.16	36.34	45.97	26.97	_	66.77			68.17	52.47	40.42	3999.00z	50.65
	0		16 07	70 73	88	67.42	72 92	71.86	63 36	52.73	41.33	31.55	52.18
MEAN	33.80	30./3	40.04	0.40	9.0	3.00	100		6	2 47	F 27	A 9.4	1 72
C V	5.60	5.53	2.21	2.25	2.94	2.90	2.83	Z.33	3.4	7.47	7.6	† ·	7
	0.35	0.40	000	-0.61	-0 22	0.79	0.0	0.38	-0.22	0.69	-1.32	96.0-	-0.70
2 2 2 2 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	0.0) (0.00	BE 24	72 03	CA 77	75 18	68 17	57 89	46.27	36.90	53.76
¥¥×	40.61	44.10	48.55	20.97	20.00	20.0	71.		- I			4	70.07
Z	23 98	26.09	42.16	50.05	55.32	63.42	68.66	68.52	57.75	49.23	29.42	22.10	17.64
YRS	6	10	o	9	10	တ	10	9	9	9	5	්	_

QUANTITY: STATION NUMBER 353847 ELEMENT:DAILY PRECIPITATION STATION:Hermiston FROM DATA WITH UNITS: INCHES a=1 day missing, b=2 days missing, c=3 days,..etc.., z=26 or more days missing, A=Accumulations present Long-term means based on columns; thus, the monthly row may not sum (or average) to the long-term annual value.

MONTHLY SUM

MAXIMUM ALLOWABLE NUMBER OF MISSING DAYS:

S

	1441	000	OVE	day	MAV	N		AliG	SEP	OCT	NON	DEC	ANN
YEAR				2 5	20	0.77	000	000	0 42	0.36	2.02	0.63	9.27
1884	5 4 .0	3 -	- -	2	40.	· ;		1 6	! ?		1	000	17.0
1985	0.25b	1.13	0.74	0.12	0. 4	0.64	0.00	0.39	1.04 40.	G. 89	J./8	0.03	0/./
1986	1.57	2 38	111	0.37	1.09	0.01	0.37	0.02	1.00	0.56	1.92	66.0	11.39
1987	1.67	0.76	1 09	0.05	0.51	0.19	0.18	0.00	0.00	0.0	0.35	1.31	5.89
1000	200	2 5	86.0	2.16	0.76	0.50	0.01	0.0	0.65	0.00	1.51	69.0	8.24
1000	, c	- 6 5 C	1 84	86.0	1.27	0.00z	0.19	0.59	0.00	0.34	1.78	0.64	9.97a
1000	769	900	0.55	96.0	0.00	0.28	0.15	0.74	0.00	96.0	0.50	0.07d	5.26a
1990	9 6	0.43	000	000	0000	0000	0.00z	0.00z	0.00z	0.00z	0.00z	0.00z	0.67k
1661	200	5 6	0.00	1 88	000	0.71	0.27	0.13	0.39	0.61	1.19a	1.31	6.30c
786L	0.007	0.002	70.0	3	9 6	- (100	9 6				a	880
1993	1.88b	1.61	1.32	0.98	0.83	1.06	0.34	0.63	0.02	0.32	9 0.0	0.00	9.00
1994	0.79a	0.97	0.08	0.24	2.48	1.60	0.25	0.00	0.14	0.98a	1.83	0.00z	9.36a
MEAN	1 05	00	101	0.86	06.0	0.64	0.18	0.25	0.37	0.50	1.30	0.79	8.74
	2 . 0	90.0		900	0.73	0.48	0.14	0.30	0.41	0.36	0.72	0.38	1.89
O.D.	8 6	9 9	-0.27	5.5	86	0.67	-0.12	0.57	0.65	00.00	-0.65	-0.19	-0.13
SAEV	5 6	3 6	7 7	. c	2 48	1 60	0.37	0.74	1 04	0.98	2.02	1.31	11.39
MAX	00.	6.30	- C	- i	9 6	- 6					000	70.0	5 89
Z	0.25	0.01	0.08	0.02	0.03	0.0	0.00	0.00	0.0	3.5	S)) (
YRS	6	10	တ	9	თ	တ	9	9	9	9	20	5 0	ø

			Evapo	ration	Jata fo	r Hern	Evaporation Data for Hermiston, OR	OR				
Station Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
35 3847 TEVP HI 1975	6666	6666	329B	521	834	964	1114	917	627	6666	6666	6666
35 3847 TEVP HI 1976	6666	6666	6666	488	823	626	1095	745	616	6666	6666	6666
35 3847 TEVP HI 1977	6666	6666	335	658	749	1033	1181	991	207	6666	6666	6666
35 3847 TEVP HI 1978	6666	6666	363B	401	803	1019	1127	918	561	6666	6666	6666
35 3847 TEVP HI 1979	6666	6666	457B	499	784	974	1191	947	638	6666	6666	6666
35 3847 TEVP HI 1980	6666	6666	395B	598	902	831	1088	964	655	6666	6666	6666
35 3847 TEVP HI 1981	6666	6666	355	572	807	882	1101	951	638B	6666	6666	6666
35 3847 TEVP HI 1982	6666	6666	364B	548	870	953	1177	1000	533	6666	6666	6666
35 3847 TEVP HI 1983	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666
35 3847 TEVP HI 1984	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666
35 3847 TEVP HI 1985	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666
35 3847 TEVP HI 1986	6666	6666	6666	296	787	1096	1051	1034	569	6666	6666	6666
35 3847 TEVP HI 1987	6666	6666	344	592	962	955	1073	1041	756	6666	6666	6666
35 3847 TEVP HI 1988	6666	6666	6666	511	769	888	6666	6666	6666	6666	6666	6666
35 3847 TEVP HI 1989	6666	6666	6666	6666	784	6666	1222	1013	669	6666	6666	6666
35 3847 TEVP HI 1990	6666	6666	6666	636B	794	1055	1189	935	676	6666	6666	6666
35 3847 TEVP HI 1991	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666
35 3847 TEVP HI 1992	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666	6666
Mean	0	0	3.67	5.517	7.93	9.657	11.34	9.546	6.229	0	0	0
SD dev			0.41	0.717	0.398	0.766	0.554	0.785	0.714			
max			4.57	6.58	8.70	10.96	12.22	10.41	7.56			
min			3.29	4.01	7.06	8.31	10.51	7.45	5.07			
years			8	12	13	12	12	12	12			